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WIGGIN ALLOYS LTD. HEREFORD (ENGLAND)

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DEVELOPMENT OF A BRAZING ALLOY FOR THE MECHANICALLY ALLOYED H16--ETC(U)

SEP 81 W E MORGAN; P J BRIDGES

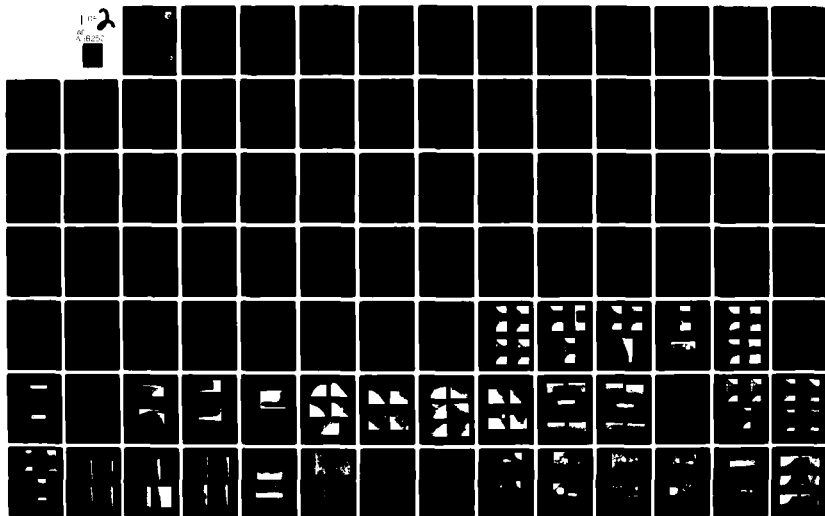
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DEVELOPMENT OF A BRAZING ALLOY FOR THE MECHANICALLY ALLOYED
HIGH TEMPERATURE SHEET MATERIAL INCOLOY ALLOY MA 956

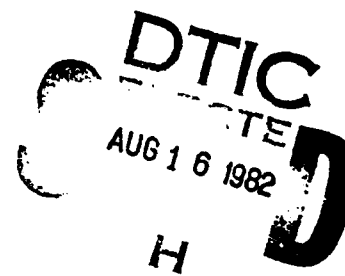
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Wiggin Alloys Limited
Hereford, England

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WILLIAM A. BAESLACK III
Structural Metals Branch
Metals and Ceramics Division

FOR THE COMMANDER



GAIL E. EICHELMAN
Chief, Structural Metals Branch
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This report describes trials on a range of potential brazing alloys for use on the mechanically alloyed high temperature ODS material INCOLOY MA 956 at temperatures up to 1200°C. Brazing properties were assessed on an initial 60 compositions chosen on the basis of melting point and substrate compati- bility, from the Ni-Cr-Pd, Fe-Cr-Pd, Ni-Cr-Ge, Fe-Cr-Ge, Fe-Cr-B and Fe-Cr-Si ternary systems. The only one of these which proved to be satisfactory in terms of brazing characteristics, oxidation resistance and strength at 1100°C was the Ni-Cr-Pd system. On the basis of cost the Ni-44 Cr-12 Pd base was		

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Block 20. Abstract (Continued)

chosen for further alloying with W, Mo, Al and/or Si. These elements were added with the aim of enhancing the high temperature mechanical properties by solid solution strengthening. In general these quaternary (etc.) alloys had melting points above 1200°C and acceptable brazing characteristics but a meaningful comparison of their mechanical properties with each other and with commercially available alloys was not possible because of large amounts of porosity in the test lap joints. This porosity was due to the fact that the experimental braze alloys could only be prepared in the form of comminuted turnings and, before any valid comparison can be made, it is necessary to obtain foils of the alloys which can be used, hopefully, to make sound joints. This work is still in progress.

Static and cyclic oxidation tests at 1100°C showed that the Ni-Cr-Pd alloys containing 5-10% tungsten had the best properties of the experimental brazes, comparing favourably with commercial alloys.

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PREFACE

This Final Technical Report documents work performed by Wiggin Alloys, Hereford, England under USAF Contract F49620-79-C-008 for the period 1 December 1978 to 31 March 1981.

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Mr. W. E. Morgan was the Principal Investigator with Dr. P. J. Bridges (INCO European Research and Development Centre, Birmingham, England) also contributing to the work reported herein.

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SECTION 1

INTRODUCTION AND PROGRAMME OBJECTIVE

Nickel and iron based mechanically alloyed oxide dispersion strengthened (ODS) materials have been developed in recent years to provide increased temperature capability over the conventional precipitation hardened alloys. Numerous potential applications exist for the new materials in aerospace and power generation plant but it is well established that joining these alloys by conventional fusion welding techniques has presented problems, especially in achieving good quality high temperature joint properties, mainly because of agglomeration of the dispersoid in the weld bead. Brazing, diffusion bonding and transient liquid phase bonding are considered the most appropriate joining techniques with brazing offering the most potential, especially for more complex joint configurations.

Although there are several high temperature brazing alloys available for superalloys which exhibit good brazing characteristics and produce joints with properties approaching those of the base metals, commercial braze products have to date generally shown limitations when used with the latest ODS alloys containing high aluminium levels for improved oxidation resistance. Mechanically alloyed materials can also under certain circumstances contain small residual amounts of inert gas which can be released into a brazed joint causing porosity. Our experience at Wiggins Alloys Ltd., has shown that the degree of porosity is related to the severity of base metal erosion occurring during brazing. Such porosity has been found to be most severe in joints produced with commercially available nickel base brazes alloyed with melting point depressants such as silicon and boron.

A currently produced mechanically alloyed iron based sheet material, INCOLOY alloy MA956, has excellent high temperature strength and corrosion resistance and has several potential aero-engine applications in flame tubes, stator blades, after burners, etc. If the high temperature capability of this material is to be exploited to the full, brazed joints must have the ability to withstand service temperatures in the general range of 1100 - 1250°C. It follows that a braze melting temperature of 1200 - 1300°C is required. A brazing alloy is therefore needed with good strength, ductility and oxidation resistance at these high service temperatures; further, the alloy must not give excessive base metal erosion during the high temperature brazing operation.

Currently available high temperature braze metals, TD-6 and TD-20, the compositions of which are given in Table 1 together with that of MA956, were developed for use with TD Nickel and are considered to show deficiencies, especially in respect to joint integrity, when used with MA956.

The objective of this project was to examine a range of potential braze alloy compositions with respect to their brazing characteristics and high temperature mechanical and corrosion properties with a view to identifying commercially viable materials superior to those currently available.

The original proposal divided the work into five phases. However, the content of the last two phases has changed from the plan because of experimental problems in obtaining porosity free joints. This final scientific report divides the work carried out into four phases, each of which is reported in a separate section. These are preceded by a section describing how the trial compositions were selected.

SECTION 2

ALLOYING APPROACH AND RATIONALE

2.1 APPROACH TO PROBLEM

High temperature brazing alloys are generally either based on Nickel (e.g. Ni-Cr-Si-B, Ni-Cr-Si, Ni-Si-B, Ni-P-B) or the noble metals (e.g. Au-Ni-Pd); both groups of alloys have good high temperature strength and oxidation resistance. The main disadvantage of the nickel based alloys with melting point depressants such as Si, B etc., is that they are generally of low ductility and react excessively at the brazing temperature envisaged for Alloy MA956, causing erosion and base metal penetration. The noble metal brazes are by contrast generally ductile and, therefore, producible in wire and foil form as opposed to powder. Alloys such as 70 Au-22 Ni-8 Pd are, however, very expensive.

It was clear that none of the currently used alloys was satisfactory for brazing Alloy MA956 and a new material had to be developed if the full high temperature potential of this material was to be exploited.

In developing a suitable braze alloy the following properties were to be aimed at:

1. Good brazeability with a brazing temperature in the range 1200 - 1300°C.
2. Oxidation resistance as near as possible to INCOLOY alloy MA956 and preferably superior to existing braze materials such as TD6 and TD20.
3. Good high temperature tensile and creep rupture properties.
4. Minimum amount of base metal erosion.
5. Relatively stable microstructure with minimum inter-diffusion effects after exposure.
6. Preferably the brazing alloy should be workable to foil or wire. However, this was regarded as of secondary importance since the majority of currently established materials are used in powdered form.

2.2 SELECTION OF SUITABLE ALLOY BASES

2.2.1 General Considerations

As previously discussed, Si and B additions have formerly been necessary to depress the melting point of nickel-base alloys to a suitable brazing temperature (e.g. 1000 - 1150°C). These elements result in brittleness and

base-metal erosion in nickel alloys, although Si is generally beneficial to oxidation resistance. The new requirements of a brazing temperature in the approximate range of 1200 - 1300°C permitted re-appraisal of the nickel-base systems which have previously been rejected, and which may be free from the disadvantage of systems in current use. Iron-base systems have also previously been rejected because their melting points are generally even higher than those of nickel-base alloys. These were also re-appraised, particularly since it seems generally sound sense to use an iron-base braze with a iron-base M.A. material, thereby avoiding possible problems associated with undesirable changes of composition by diffusion in service.

2.2.2 Nickel-Base Alloys

Chromium is well known to be a necessary addition to nickel for high temperature oxidation resistance. A minimum of about 20% is normally required. However, high levels of chromium (e.g. > 30%) result in alloys of poor workability and such alloys, though not ruled out of this investigation, would not be amenable to working to foil. Chromium also has the beneficial effect of forming a eutectic at 51% Cr (Ref. 1) thereby lowering the melting point of nickel progressively from 1453°C to 1345°C (Table 2). For these reasons, the nickel-chromium system has formed the basis of all the nickel-base alloys.

Palladium forms a eutectic with nickel at 1237°C and 60% Pd (Ref. 2). The liquidus temperatures for the Ni-Cr-Pd ternary system have been determined (Fig. 1, Refs. 2 and 6). A minimum liquidus temperature of ~1250°C is attainable over a wide range of compositions. This temperature falls within the brazing temperature range of interest for brazing Alloy MA956. Palladium is, unfortunately, expensive. However, many potentially useful compositions contain < 30% Pd and so the alloy could be substantially cheaper than currently established gold or palladium-base brazing alloys. Preliminary evaluation of Ni-Cr-Pd for brazing Alloy MA956 has been done at Wiggin Alloys Ltd. The braze alloys have shown good oxidation resistance, a promising freedom from porosity and base metal erosion and, in addition, good wettability. This latter feature has been suggested to be due to a lowering of the liquid braze alloy surface energy as a result of the presence of palladium (Ref. 5). It thus appeared that the Ni-Cr-Pd system was worthy of further investigation.

- Ref. 1 M. Hansen, 'Constitution of Binary Alloys', McGraw-Hill, New York, 1958.
- Ref. 2 V.A. Nemilov et al, Izvestiye Akad. Nauk SSSR, 22, (1948), 175.
- Ref. 5 W. Feduska, Welding J, 39 (1960), 292S.
- Ref. 6 D.W. Rhys et al, Metallurgia, (1962), 255.

The Ni-Ge system forms a eutectic at 1135°C and 34% (Table 2). Previous workers (Ref. 3) have considered Ni-Cr-Ge alloys for brazing. They determined approximate solidus temperatures of 980 up to 1205°C in the compositional area which they studied (Fig. 2). Clearly there is ample scope in this system to obtain alloys which melt within the desired range of 1200 - 1300°C and thus these also were studied.

2.2.3 Iron-Base Alloys

A survey of binary iron-base alloys showed that several eutectic systems exist which are of interest. Pd, Ge, Si, B, P, Sc, Ti, Zr, Be and C will depress the melting point of iron to temperatures varying from 1050 to 1310°C. However, in order to keep the work to manageable proportions, Pd, Ge, Si and B were selected since these elements form eutectic or congruent melting systems analogous to the nickel base systems (Table 2, Figs. 3-6).

Since data are available on the nickel systems, but very little is reported on the iron bases, it was felt that the similarities in the two systems would allow some degree of extrapolation of properties from the nickel brazing alloys to the iron-base systems. Careful consideration was given to the inclusion of Si and B, in view of their deleterious effect on ductility and base metal erosion, when used in nickel-base alloys. However, since these elements are the most effective in depressing the melting point, it was concluded that it would be wrong to reject them without actually testing their behaviour in iron-base alloys. Moreover, the Fe-Pd system has a minimum melting point of 1310°C and might require further depression. Small amounts of B or Si might be effective in further lowering the melting point, without having an undue effect on other properties.

As with the nickel-base alloys, chromium was considered necessary to give oxidation resistance and so iron-chromium formed the basis of all of the iron alloys. Unfortunately, chromium is not very effective in lowering the melting point of iron (Table 2). Comparison of the iron and nickel-base systems shows that Ge and B are equally effective in both alloy bases. Si and Pd result in higher melting points when alloyed with iron than with nickel. Generally, even the Ge and B - containing Fe-Cr alloys must be expected to have a higher melting point than their nickel-base counterparts, because of the relatively small effect of chromium on the melting point of iron.

Ref. 3 D. Canonico et al, Welding J. (1960), 122S.

No useful data are available on the liquidus temperature of Fe-Cr-X ternary alloys. Some ternary equilibrium diagrams have been determined for the Fe-Cr-Si system (Ref. 4, Fig. 7) together with solid solution limits and areas of σ formation but, unfortunately, not liquidus temperatures. There was clearly a need to define compositions with liquidus temperatures of interest and these were determined by differential thermal analysis (DTA).

2.2.4 Alloying Guidelines

The initial experimental alloys for phase I were selected on the following criteria:

- i) Expected liquidus temperatures predicted from ternary diagrams (nickel base alloys only) and available binary diagrams for iron-base systems.
- ii) Sufficient chromium content to give adequate oxidation resistance, given that alloying additions such as silicon will be beneficial in this respect.
- iii) Avoidance, where possible, of intermetallic phase regions.
- iv) A consideration of the economics of each system.

While some of the compositions chosen were close to potentially useful brazing alloy compositions, an important purpose of this work was to define the boundaries of areas within a given system which have useful liquidus temperatures. Therefore, some of the alloys chosen may well have higher than desirable melting points and/or undesirable alloy phases.

The plan was to cover a wide range (60) of potential ternary alloy bases in the first phase. On the basis of the preliminary tests the number would be cut to about 10 for more detailed investigations in phase 2. Further selection would then narrow the choice to two bases to which, in phase 3, quaternary (etc) additions would be made and these alloys would subsequently be further assessed in order to arrive at the best alloy.

Ref 4 A.E.H. Anderson et al, Trans ASM, (1936), 375.

SECTION 3

PHASE I INITIAL APPRAISAL OF 60 POTENTIAL BRAZE ALLOYS

The objective of Phase I was an evaluation of the melting points and brazeability of two Ni-base and four Fe-base alloy systems involving a total of 60 alloy compositions.

3.1 EXPERIMENTAL DETAIL

3.1.1 Braze Alloy Preparation

Ten alloys from each of the six alloy bases were produced as 50 g button melts in an argon arc furnace. Each button was analysed using chemical/XRF techniques; the results are detailed in Table 3. At the initial stages selected specimens were examined by EPMA techniques to confirm homogeneity.

3.1.2 Differential Thermal Analysis

A Linseis L62 differential thermal analysis unit was used to determine the liquidus temperature of the sixty alloys; the results are listed in Table 3.

3.1.3 Brazing

Small chips were machined from the alloy buttons and these were further comminuted in a pestle and mortar to a size suitable for brazing.

Each braze alloy was evaluated for its wettability by assessing the spread of approx. 0.2 g of braze alloy on a 20 mm square flat sheet sample. Braze alloy flow was assessed on a 40 mm long tee-specimen using a 0.003" braze gap. This particular gap was chosen as being representative of a likely production situation. Commercial braze alloys TD6 and TD20 were used throughout as comparators.

INCOLOY alloy MA956 as currently produced has a grit blasted surface which was found by some initial trials not to promote good braze metal flow. A number of surface conditions were evaluated and a 240 grit finish was chosen for both the braze specimens.

Brazing was carried out in the flat position in a vacuum furnace with a commercial 'Microbraz' cement binder being used to hold the brazing alloy in position. The brazing temperatures and vacuums employed are given in Table 3. The brazing temperatures chosen were in general 20 - 30 °C above the determined liquidus temperatures although in some instances higher braze temperatures were required. Subjective judgements on the appearance of the braze samples with regard to spread and flow are given in Table 3.

In general good braze metal flow and wettability was shown by alloys in the Ni-Cr-Pd, Ni-Cr-Ge and Fe-Cr-Pd systems. Variable brazeability was shown by Fe-Cr-Ge and Fe-Cr-B alloys whilst the Fe-Cr-Si system exhibited very poor brazing performances.

3.1.4 Metallographic Examination of Braze Samples

Metallographic sections were taken through both the flat and tee-specimens, the latter being sectioned approximately two-thirds of the distance along the joint from the initial placement position of the braze alloy. The flat specimens were used principally to measure contact angles with the tee-specimens being assessed for porosity and base metal erosion. In a number of samples a second section was taken to confirm that the original microsection was representative. Some variability was inevitably noted but was not considered to be excessive.

In order to compare the alloys performance a scoring system was devised which gave a measure of the quality of the brazes as seen in metallographic sections. Three digits were ascribed to each sample, each digit having a value of 0, 1, 2 or 3. The first digit gives a measure of the amount of large porosity, the second refers to small pores and the third measures the amount of base metal erosion under the braze. A zero score indicates no porosity or erosion; a score of three indicates an excessive amount of these. The results of this evaluation are given in Table 3. Measurements of porosity were made on polished sections and these were then subsequently etched to reveal the amount of base metal erosion. The soundness and erosion which occurred with braze alloys TD6 and TD20, used for comparison, are shown in Figures 8-11. General observations on each series of experimental braze alloys were as follows:-

(A) Ni-Cr-Pd Alloys

These all had potentially useful melting points (in range 1260 - 1340°C) and good flow and wetting properties. However the amount of braze metal porosity and base metal erosion was variable and on the basis of these parameters, it was only possible to find three candidate alloys for the next phase, (1A, 6A, 8A). The structure of alloy 1A, considered to be acceptable, is shown in Figures 12 and 13 whereas alloy 5A, which showed excessive porosity is shown in Figure 14.

(B) Ni-Cr-Ge

These also had potentially useful melting points (in range 1290 - 1390°C) and good flow and wetting properties. However, the amount of porosity was, in most cases, unacceptable. Two alloys were chosen for further study, (1B and 5B). The structure of alloy 1B is shown in Figure 15 whilst that of alloy 3B, which was rejected, is shown in Figure 16.

(C) Fe-Cr-Si

Although these alloys had potentially useful melting points they did not flow and, on cooling, formed cracks which sometimes propagated into the substrate. None of this series was considered suitable for further work. Figure 17 illustrates these points.

(D) Fe-Cr-Ge

Some alloys in this series had comparatively low melting points (<1150°C) and poor flow properties and were rejected on these grounds. The remainder formed reasonable braze joints with low porosity and little or no base metal erosion. However, these all contained very bad cracks and hence none from this series were suitable for further study. Representative structures are shown in Figures 18 and 19. Figure 18 relates to alloy 2 D and shows bad cracking in the braze extending into the parent sheet. Figure 19 shows bad porosity and erosion in alloy 9 D. No brazing was carried out with alloy 4D because of its excessively high melting point.

(E) Fe-Cr-Pd

The melting point range was 1320 - 1410°C and all the alloys flowed well and had good wetting properties. Porosity and base metal erosion was variable and three alloys were selected for evaluation in Phase 2 (2E, 4E and 9E). Figures 20 and 21 show the sound nature of the joint with alloy 9E.

(F) Fe-Cr-B

The melting points of these alloys were all in the range 1200 - 1260°C and a number of them flowed and produced wetted joints. There was very little, if any, porosity in the braze metal and the base metal erosion was low. Three alloys were selected for phase 2, (3F, 5F and 6F). A typical satisfactory joint, as produced with alloy 5F, is shown in Figures 22 and 23.

3.2 SELECTION OF ALLOYS FOR PHASE 2

In the proposed programme a minimum of 8 alloys were to be selected for further evaluation in Phase 2. Based on wettability, flow, porosity and base metal erosion, eleven alloys were selected for this phase. These alloys are listed in Table 4. The two baseline alloys, TD6 and TD20, were also carried forward into this phase.

The task of choosing individual alloys from the Ni-Cr-Pd series proved difficult because several alloys showed similar characteristics. It was not possible to correlate alloy composition with braze performance although following discussions with EOARD/MOD personnel the melting range of the alloys was to be examined to determine if this correlated with braze performance. Meanwhile, the alloys for Phase 2 were selected on the basis of good brazeability and soundness and covering a wide spread of compositions.

In the Ni-Cr-Ge series there was a tendency for erosion to increase with Ge content. Only two alloys from this series were selected and these both had nominally 5% Ge.

For the Fe-Cr-Pd system the three best alloys were chosen from a generally good series.

All the alloys in the Fe-Cr-B series showed low porosity and erosion and the main factors in choosing the three compositions for further study were braze flow and sufficiently high Cr level to develop the necessary oxidation resistance.

One problem known to exist in brazing alloy MA956 is braze metal porosity. The commercially available alloys TD6 and TD20 have shown significant porosity and whilst the eleven alloys selected for further evaluation were not pore-free, they were superior to TD6 and TD20. A limited number of samples tested have shown improved wettability on nickel-plated surfaces and it was of interest to note if these samples also showed reduced porosity levels. If proved to be the case, it could be necessary to re-assess the work programme. However, from a practical fabrication standpoint the necessity for nickel plating must prove undesirable.

3.3 RESEARCH PLANNED FOR PHASE 2

Tensile and stress-rupture specimens would be produced as close as possible to the AWS Specification C3.2-63/60.105. Tensile and stress rupture tests would be carried out at 1100°C with a minimum of 2 stress rupture and two tensile samples per alloy. The integrity of the lap points would be checked by X-ray examination prior to testing.

Cyclic oxidation tests in air between room temperature and 1100°C would be carried out on lap brazed joints. Performance would be evaluated by metallographic examination.

Microstructural stability of the alloys would be determined for each alloy by a 1000h/1100°C heat treatment and metallographic examination.

SECTION 4

PHASE 2 FURTHER EVALUATION OF ELEVEN ALLOYS SELECTED FROM PHASE 1

The alloys examined in Phase 2 are listed in Table 4. Two commercially available brazing materials initially developed for thorium dispersed nickel, TD6 and TD20, were also included in the tests.

4.1 EXPERIMENTAL DETAILS

The eleven experimental braze alloys listed in Table 4 were melted as 50g buttons in an argon-arc furnace, machined to chips and further comminuted to size for brazing as in Phase 1.

4.1.1 Mechanical Tests

Tensile and stress-rupture blanks were vacuum brazed essentially as per AWS specification C3.2-63/60.105. The test piece used had small dimensional variations from this standard and is shown in Figure 24. The blanks were brazed vertically and some difficulties were experienced in retaining braze metal at the joint due to vibration of the furnace. This problem was overcome by tacking on a small retaining foil to hold the braze in place. This foil was removed during the subsequent machining of the test-piece. All brazed blanks were X-rayed prior to machining to check the joint integrity. 1100°C creep rupture and tensile tests were carried out in air, the latter employing a cross-head speed of 2.5 mm/min. Prior to testing the boron containing alloys were given a diffusion treatment under argon of 4h/980°C, this procedure being used commercially with the boron containing AWS B Ni-1a alloy.

4.1.2 Isothermal Exposure

Small beads (approx. 0.2g) of braze alloy, deposited on MA956 sheet samples were thermally exposed in air for 1000h/1100°C. Metallographic examination of the samples was carried out to assess isothermal oxidation characteristics.

4.1.3 Cyclic Oxidation

The intrinsic cyclic oxidation resistance of the alloys was assessed by testing small discs of pure braze metal taken from the original eleven 50g button melts. Similar discs were also taken from TD6 and TD20 braze melts made under vacuum in small ceramic cups. Exposure was carried out in air for 300h, the cycle consisting of 20 min at 1100°C followed by 10 min at room temperature, i.e. two complete cycles per hour. Samples were subsequently examined metallographically to assess the degree of oxidation.

4.2 RESULTS OF TENSILE, CREEP RUPTURE AND OXIDATION TESTS

The results of the tensile and stress rupture tests at 1100°C in air are given in Tables 5 & 6 respectively together with an assessment of the braze porosity taken from X-ray pictures. Two typical X-rays are shown in Fig. 25. The shear stress at failure on the braze was calculated using:-

$$\text{Shear stress} = \frac{\text{applied load}}{\text{width of point x overlap}}$$

These parameters were measured for each test piece since inevitably there were small variations in joint measurements from those specified in the AWS specification. The failure mode in each sample is also given in Tables 5 & 6.

With regard to the failure mode of the test samples it should be noted that most failed in the MA956 sheet rather than in the braze. This was caused by re-alignment of the sample during testing as illustrated in Fig. 26. Thereby a combination of bending and tensile stresses was imposed on the MA956 at the end of the overlap and fracture occurred there. However, some samples did fracture within the braze metal or at the braze/MA956 interface. A cross-section of each type of failure is shown in Figures 27-31.

Sections of the brazes after 1000h isothermal exposure in air at 1100°C are shown in Figures 32-41 and the results summarised in Table 7. No results are given for the three boron containing alloys (F series) because, in preliminary atmospheric exposure trials, they evolved a volatile compound which contaminated the other samples and rapidly corroded any adjacent exposed MA956.

Sections of ten of the brazes after 312h thermal cycling (1100°C - R.T.) in air are shown in Figures 42-51 and the results are summarised in Table 8. The three alloys not shown are the boron containing series, (3F, 5F and 6F) which were all completely oxidised in 24h in this test.

4.3 DISCUSSION OF PHASE 2 RESULTS

The tensile test results were not particularly useful in identifying brazing alloys with superior properties. Although there was considerable variation amongst the results there is no series which was consistently good. There were also complications imposed firstly by the unavoidable porosity in some samples and secondly by the bending of the test sample at the end of the overlap and subsequent tendency for failure to occur there rather than in the braze. The tensile test results were therefore more of a measure of the MA956 properties than of the braze properties.

On the topic of braze porosity an examination of the DTA results from Phase I failed to show any correlation between melting range and braze metal porosity.

The stress rupture results show more tendency to group themselves according to the type of braze and there were also more failures within the braze rather than in the MA956 sheet. The two bases containing palladium (A series Ni-Cr Pd and E series Fe-Cr-Pd) had the best stress rupture lives. Both the Ni-Cr-Ge and the Fe-Cr-B alloys were poor. The latter alloys evolved a volatile compound which corroded nearby MA956 and induced premature failure (Fig. 31) even after a prior diffusion treatment of $\frac{1}{2}$ hr/980°C/argon.

The TD-6 and TD-20 also gave poor results but it proved very difficult to make sound brazes with these alloys within limitations imposed by the brazing rig.

From an oxidation standpoint the more exacting but shorter term conditions of the cyclic oxidation test showed the Ni-Cr-Pd alloys to be the best of the experimental alloys, being about equivalent to the two commercial alloys TD6 and 20. The Ni-Cr-Pd alloys all showed an adherent scale with reasonable spalling resistance in the cyclic test. The alloy with the lowest Cr level, 8A (32 Ni-20 Cr-48 Pd), showed the most oxidation under cyclic and isothermal conditions and there appears to be an advantage in keeping the Cr level high in these alloys, although the 44% Cr material, 1A, did show some interdendritic oxide penetration in the cyclic test.

In the Ni-Cr-Ge series the slightly higher (40%) Cr level of alloy 5B did not appear to confer any improvement in oxidation resistance over alloy 1B (35% Cr). Alloy 5B did not, however, oxidise as heavily under cyclic conditions as under isothermal conditions. In the cyclic test both alloys performed reasonably well but did not have such an adherent oxide film as the Ni-Cr-Pd alloys.

The Fe-Cr-Pd alloys all showed loose, friable scales and significant oxidation in the cyclic test. The highest Cr member of this series, 2E (35 Fe-25 Cr-40 Pd), was least affected under isothermal conditions and showed the least spalling in the cyclic test.

The three Fe-Cr-B alloys showed little cyclic oxidation resistance at 1100°C, being completely oxidised in 24h.

4.4 SELECTION OF ALLOYS FOR PHASE 3

The most promising alloys appeared to be at the high chromium end of the Ni-Cr-Pd series. Alloy 1A (44 Ni-44 Cr-12 Pd) had good oxidation resistance and relatively good stress rupture properties when compared with other bases and it was proposed that this alloy should be investigated further. Alloy 6A was also considered to be worthy of further evaluation. It showed good oxidation resistance and stress rupture properties. It does, however, have a relatively high (30%) palladium content which makes it expensive.

One of the aims of the project in the original proposal was that an iron containing base should be carried through to Phase 3. In this respect alloy 2E (40 Fe-20 Cr-40 Pd) was worth further consideration. However, its oxidation resistance did not match the commercial brazes TD6 and 20 and therefore it was considered worthwhile trying alloy 8E (15 Fe-35 Cr-50 Pd) also. This latter alloy was rejected after Phase 1 because it had marginally more small pores in it after brazing than 2E but it does have a higher chromium content which should aid corrosion resistance. Both the suggested E series alloys have the cost disadvantage of a high palladium content.

The Fe-Cr-B alloys did not appear to offer much prospect for development. There is a problem of volatile corrosion products which are formed on heating in air and even after a suitable diffusion treatment the stress rupture properties of the brazes were poor. There could be scope for overcoming these problems by using thinner braze layers and/or other diffusion treatments but this course would not be within the scope of the project.

Similarly the Ni-Cr-Ge alloys were not considered to be very promising. Although 1B had good high temperature corrosion resistance its stress rupture properties were poor. Alloy 5B had poor stress rupture properties and variable performance in the oxidation tests.

Phase 3 involved making quaternary etc alloying additions to the chosen ternary bases from Phase 2 with a view to further improving high temperature properties without adversely affecting brazing capabilities. Therefore any proposed strengthening addition should not raise the brazing temperature above what would be a reasonably practical upper limit, say about 1350°C.

The alloying additions under consideration were tungsten and molybdenum which should improve high temperature strength and silicon which should aid flow properties and oxidation resistance. A series of alloys of the following compositions (based on alloy 1A) appeared suitable for further evaluation, their melting points to be determined by DTA as no phase diagrams were available.

		Cr	Ni	Pd	W	Mo	Si
1A	- 1	44	40	11	5	-	-
	- 2	44	36	10	10	-	-
	- 3	44	40	11	-	5	-
	- 4	44	36	10	-	10	-
	- 5	44	42	12	-	-	2
	- 6	44	34	10	5	5	2

If the melting points proved to be in the right range and there were no other obvious problems involved in melting these alloys they would be more fully investigated under the programme laid down for Phase 3. Similar alloys based on 8E (Fe-Cr-Pd) would also be considered.

One problem which became obvious at this stage was the design of the mechanical test sample. If the properties of the brazes were to be measured and compared reliably then the problem of bending and failure in the MA956 sheet had to be overcome. Other test piece configurations were possible (Fig. 52) and the double lap specimen seemed worthy of evaluation.

SECTION 5

PHASE 3 ASSESSMENT OF QUATERNARY (ETC) ALLOYS

5.1 INTRODUCTION

This section describes the progress made under the following three headings and also reports results of optical metallography and microprobe analysis carried out to assess the long term stability of selected brazes.

- 1) Select and prepare a range of quaternary alloys based on Ni-Cr-Pd and Fe-Cr-Pd, measure their melting points, oxidation resistance, brazing properties and, after appropriate selection, braze strengths.
- 2) Assess the modified double lap mechanical test sample which was designed to eliminate bending and subsequent failure in the MA956 rather than, as required, in the braze under test.
- 3) In an attempt to overcome the bad porosity prevalent in brazes made with TD-6 and TD-20 a prior de-aluminising treatment would be given (by D. Becker/AFML) to the MA956 coupons.

5.2 EXPERIMENTAL DETAILS

5.2.1 Alloy Selection

With regard to a nickel base material, it was concluded from the earlier work that alloy 1A (44 Ni-44 Cr-12 Pd) was the best to explore further on the basis of its brazing properties, strength, corrosion resistance and cost. Therefore this base was alloyed with W, Mo, Si and Al. For an iron-containing braze alloy 8E (15 Fe-35 Cr-50 Pd) was chosen because it had the best combination of melting point, brazing properties and chromium content, this latter parameter being relevant to obtaining good corrosion resistance.

The alloys investigated in the present phase are listed in Table 9. They were prepared as 50g button melts in an argon arc furnace, machined to chips and further comminuted to size for brazing as reported previously.

5.2.2 Brazing Trials

Test pieces were prepared from each braze, as in Phase 1 using coupons of MA956, ground to a 240 grit finish, to form T-pieces and flat spread samples. Visual assessments of flow and wettability were made from these coupons which were then section by spark machining and used to

measure contact angle, base metal erosion and braze metal porosity. Results of these observations are given in Table 10 along with the braze metal melting point as measured by DTA and the brazing temperature and conditions used. The scoring system used in assessing porosity and erosion was the same as that employed previously (Phase 1). Typical sections of the brazes are shown in Figs. 53-58.

5.2.3 Oxidation Tests

Samples were cut from the button melted alloys and exposed for 1000 hrs at 1100°C in air. The depth of oxide penetration was measured in metallographic sections taken perpendicular to the exposed surface and the results, together with any other relevant observations, are recorded in Table 11. Sections of the exposed brazes are shown in Figs. 59-69.

5.2.4 Mechanical Tests

Many attempts were made to produce sound double-lap joints suitable for mechanical testing. Braze temperatures up to 200°C above the determined melting point were used together with joint gaps from 0.002 to 0.010 in. and brazing times of 2-15 minutes. Despite varying these parameters it was not possible to produce a series of samples of sufficient integrity to be meaningfully mechanically tested. It appeared that with the braze alloys in the form of coarsely comminuted chips, there was insufficient joint flow and wetting. Figure 70 compares the radiographs of a double lap joint with experimental alloy 1A with a sound joint produced from commercial alloy BNi-1a in the form of a prepared ductile foil.

5.2.5 Modification of stress-rupture test piece

Test pieces were made using the double overlap sandwich configuration proposed in Phase 2. Braze alloys were taken from the Phase 2 series and the aim of the limited number of tests was to determine if the same order of merit was found for the alloys as was obtained with the previous single overlap samples. The results are listed in Table 12.

5.2.6 Surface Treatment of MA-956

In order to produce sound brazes with commercial alloys TD6 & TD20 it was considered useful to assess the effects of reducing the surface alumina level of the sheet to aid wetting. Samples of MA956 were surface treated by AFML in conjunction with the University of Dayton but little success was achieved in 'de-aluminising' the samples. A technique which had given success on Ni base materials did not prove successful on the Fe based MA956.

5.2.7 Structural Studies

As the choice of alloy bases was narrowed down there was a need to investigate in more detail the microstructure and microanalysis of the brazes both after joint preparation and also after extended exposure at elevated temperature. This would give information on interdiffusion of major elements, braze metal dilution and phase stability. Studies were made on a nickel base braze (1A-4 Ni, 44 Cr, 12 Pd) and an iron base one (4E-40 Fe, 20 Cr, 40 Pd).

(a) Alloy 1A (44 Ni-44 Cr-12 Pd)

This braze, used in a T-joint, is shown before and after 1000 hr exposure at 1100°C in Figs. 71 and 72 respectively. There is a 2-phase structure which is as expected from the equilibrium diagram (Fig. 75) and not surprisingly the second phase coarsens considerably during exposure.

The composition of the matrix and second phase before and after exposure were determined by microprobe analysis.

	Ni	Cr	Pd	Fe	Al	
AS-BRAZED	39	38	7	14	2	Matrix
	34	34	13	3	16	2nd Phase
AFTER 1000 hr/1100°C	2	20	-	72	6	Matrix
	3	7	63	5	22	2nd Phase

These analyses were made at approximately the centre line of the braze and there were variations in composition near the interface with the MA-956 in the as-prepared sample. However the results clearly show that, firstly, considerable amounts of iron, and to a lesser extent aluminium, are introduced into the brazing alloy by base-metal erosion. Secondly, during extended 1100°C exposure most of the nickel diffuses out of the braze into the adjacent MA-956 and is replaced by iron from the same source. All the detectable palladium concentrates into the second phase and the chromium diffuses into the MA-956 until the level in this and the braze are the same (~20%). Thus the composition of the braze after exposure is very different to that of the starting material.

(b) Alloy 4E (40 Fe, 20 Cr, 40 Pd)

Figs. 73 & 74 show the 4E joint before and after exposure. Once again the braze alloy is 2-phase. The Fe-Cr-Pd equilibrium diagram is not well

documented but there are various intermetallic compounds along the binaries (Fig. 76), which indicate that the ternary alloy would be complex.

After exposure the matrix phase of alloy 4E and the MA956 appear to be continuous and no real interface is present, (Fig. 74), apart from an increase in volume fraction of the second phase. The continuous nature of the two components is confirmed by the microprobe analysis.

	Cr	Fe	Al	Pd	
AS-BRAZED	22	74	4	-	MA 956
	27	62	1	10	Braze matrix
	5	8	14	73	2nd Phase
AFTER 1000 hr/1100°C	20	76	4	-	(MA 956
					(Braze matrix
	1	5	18	76	2nd Phase

The results show that the braze metal dilution and homogenisation of composition after exposure which was seen in 1A is also occurring in 4E.

5.3 DISCUSSION OF RESULTS ON QUATERNARY (etc) ALLOYS

The results suggested that none of the iron base (8E series) alloys were worth further examination. 8E-1 and 8E-2 formed unacceptably thick non-adherent oxide scales during exposure which did not appear to inhibit further oxidation. 8E-3 formed a scale which did not stay on the surface but somehow sublimed or fell off leaving fresh metal surface to be oxidised. 8E-4 and 8E-5 could not be made to flow properly, even at 1400°C which is considered to be above a practical brazing temperature.

Of the nickel base (1A series) brazes alloy 1A-4 (10% Mo) cracked easily and could therefore be rejected. Further selection on the basis of braze quality was considered to be suspect because of the non-reproducible method of preparation using powder or turnings and the possible variation in porosity level along the length of the T-joints.

The oxidation results suggested that 1A-8 (3% Al) could be abandoned because the sub-surface damage extended to 800µ depth which was over double that in any other alloy. Alloy 1A-9 (5W, 5 Mo, 1 Al, 1 Si) had the best oxidation resistance whilst there was not much difference between the others in the 1A series.

In considering the oxidation results of Phase 3 it was not possible to compare them directly with those in Phase 2 since the latter tests were done on brazed joints and not on

samples of pure braze alloy from argon arc furnace buttons.

5.4 RESEARCH PLANNED FOR PHASE 4

As stated above, it was not found possible, using the present production route with braze metal turnings, to make tensile and stress rupture test pieces which were free of pores in the braze. The next phase of the work therefore would attempt to find a method of fabricating the test alloys to thin strip which could then, hopefully, be used to prepare sound joints. Once this was done the tests planned for Phase 4 would be done on the following alloys, in the order of priority shown, to an extent which was consistent with the time scale and funds available.

1A-9	Ni-Cr-Pd-5W-5Mo-1.5Al-1.3Si
TD-6)	commercial (22Cr-17Mo-4Si-5W-bal Ni
TD-20)	alloys (16Cr-25Mo-4Si-5W-bal Ni
1A - 2	Ni-Cr-Pd-10W
1A - 3	Ni-Cr-Pd-5Mo
1A - 5	Ni-Cr-Pd-2Si
1A - 1	Ni-Cr-Pd-5W
METGLAS*	BNi-1a (ni-15Cr-3Fe-4.5Si-3B)

Alloys 1A-6 and 7 had been rejected because during braze joint preparation there would be contamination by aluminium from the MA956 and the effect of this would mask the effect of any aluminium added to the original braze metal. The commercial METGLAS BNi-1a ductile foil has been included as a comparator alloy known to give sound joints in MA956 at a braze temperature of 1175°C.

Results from the redesigned stress rupture test piece gave the same order of merit for the brazes as the single overlap samples. However fracture was still occurring in the MA956 rather than in the braze in some tests and this could be caused by the notch sensitivity of the parent sheet. It was felt that, provided there were no fabrication problems, future tests should still be done on the double overlap sample.

* Trademark of Allied Chemical

SECTION 6

PHASE 4 OXIDATION TESTS AND LIMITED MECHANICAL PROPERTY ASSESSMENT ON SELECTED ALLOYS

6.1 INTRODUCTION

As detailed previously a full mechanical property assessment of the experimental Ni-Cr-Pd braze alloys was not possible due to the unsound nature of joints produced with the alloys in the form of turnings or coarse powder. Braze alloys in the form of thin foil are being produced which will hopefully give joints without the voidage experienced hitherto.

However the AFML funded part of the project and the time scale has expired before foil has been produced and therefore this final section reports the remaining results obtained on joints made from turnings. These results are from isothermal and cyclic oxidation tests and a limited number of stress rupture tests, all at 1100°C. The compositions of the alloys tested are given in Table 9.

6.2 EXPERIMENTAL DETAILS AND RESULTS

6.2.1 Isothermal Oxidation Tests

Sample lap brazes were exposed for 1000 hrs at 1100°C in air. Typical cross sections of the exposed brazes are shown (unetched) in Figs. 71-80. There was very little oxidation at the surface of any of the samples except 1A-3. This contained gross porosity which was present before exposure (Fig. 79). Some level of porosity was present in most of the samples after preparation and this is an undesirable feature of joints made using braze metal in the form of turnings or powder.

In places where braze metal was in contact with both sides of the joint the interface appeared to be sound (Figs. 81 and 82). The 1000 hr exposure did not seem to produce either any further porosity or any deleterious phases. There was a general coarsening of the grain structure together with a corresponding growth of any second phase particles present (Figs. 84 and 86).

Samples 1A-3 and 1A-9 were examined by microprobe analysis before and after exposure to ascertain how the major alloying elements (Ni, Fe, Cr, Pd) had diffused. Both these alloys had a 2-phase structure and the results given below are taken from regions away from the diffusion zone which, in the as-prepared joints, was about 200 µm wide. (All results corrected and normalised to 100% and ignore Aluminium).

Sample 1A-3

	% Ni	% Fe	% Cr	% Pd	
As-Brazed	1.2	77.5	21.3	0	MA956 Sheet
	24.2	48.6	25.7	1.5	Braze Matrix
	5.8	10.4	6.0	77.8	Braze 2nd Phase
1000h/1100°C	1.3	69.6	29.1	0	MA956 Sheet
	1.4	69.0	29.6	0	Braze Matrix
	0	11.4	4.0	84.0	Braze 2nd Phase

Sample 1A-9

	% Ni	% Fe	% Cr	% Pd	
As-Brazed	0	77.1	22.9	0	MA956 Sheet
	12.4	46.6	39.5	1.5	Braze Matrix
	31.7	9.6	9.1	49.5	Braze 2nd Phase
1000h/1100°C	3.8	73.4	22.8	0	MA956 Sheet
	3.8	73.4	22.8	0	Braze Matrix
	13.3	0	3.0	83.7	Braze 2nd Phase

6.2.2 Cyclic Oxidation Tests

Using lap joint specimens 1000h cyclic oxidation tests were carried out at 1100 C on brazes 1A1, 1A2, 1A3, 1A5, 1A9 and commercial alloys BNi-1a, TD6 and TD20. The thermal cycle used was 20 min at temperature followed by 10 min cooling in air, i.e. two cycles per hour.

Figures 87-102 show representative sections through these lap joints before and after exposure and illustrate the level of as-brazed porosity which occurs with the various brazes. The soundest as-brazed joints were with commercial foil of the BNi-1a composition, followed by experimental alloy 1A3. Another feature readily apparent was the level of porosity developed in the parent sheet in the braze area after exposure. Only the joint brazed with BNi-1a foil was clear in this respect. As for the level of oxidation undergone by the brazes the least attack occurred on commercial alloy TD6, with alloys 1A1, 1A2 and BNi-1a the next best. The heaviest oxidation had occurred on alloys 1A3 and 1A5.

6.2.3 Stress Rupture Tests

Since it has not proved possible to obtain the experimental braze alloys in the form of foil during the present phase it was decided to test a few of the joints prepared using powder or turnings. Prior to testing these joints were radiographed and from the resulting film a rough measure was made of the porosity

present. It was hoped that allowing for the porosity the alloys could then be placed in a rough order of merit based on the stress rupture results obtained.

The test samples used were the vacuum brazed double lap joints described previously in Phase 2. The thickness of the braze layer was set at 0.1 mm by tack-welding the pieces of MA956 together before brazing. The total area of the braze was measured and hence the load required for a constant shear stress (initially 3 N/mm^2) calculated. For those samples which had lives in excess of 400 hrs at 1100°C the load was progressively increased as shown in Table 13 which lists all the stress rupture results together with the amount of porosity measured in each sample. At least two test pieces were made from each of the three alloys tested 1A3, 1A5 and 1A9. Joint porosity was so bad with alloys TD6 and TD20 that no testing was carried out.

The results show a considerable amount of scatter even after allowing for variations in the amount of porosity. From the very limited number of results it could be deduced that an order of merit of the three alloys tested is

1A-3
1A-9
1A-5

but this would need to be validated by more tests using foil material, when it becomes available, for preparing the joints.

6.2.4 Production of Braze Alloy foil

The most promising technique for making thin foil is the melt spinning of the trial brazes. This method, which is used for making amorphous alloys, melts, by induction heating, a small ($\sim 5\text{g}$) sample in a glass tube with a small rectangular orifice at the bottom. Immediately beneath the orifice is a rapidly rotating cooled copper wheel onto which the molten metal falls and is thrown off as a rapidly quenched thin ribbon.

Initial trials, at Sheffield University, produced a narrow 2 mm wide ribbon but the surface finish was not very smooth and there was some slight surface oxidation, probably due to the fact that there was no protective atmosphere around the molten metal.

Further trials were conducted on similar apparatus at Cambridge University where the spinning was done in a helium atmosphere. This improved the surface finish but the foil was undesirably narrow.

Having ascertained that the braze alloys show potential for being formed into foil by this rapid solidification process trials have been instituted at Allied Chemicals, New Jersey, U.S.A., who prepare such foils commercially.

6.3 COMMENT ON PHASE 4 RESULTS

This section covered the oxidation and limited creep rupture tests carried out since the last phase. For a satisfactory creep rupture assessment of the alloys sound joints are essential and to this end Allied Chemicals, New Jersey, are currently attempting to produce ductile foil in certain of the alloys. From an oxidation resistance standpoint only alloy LA3 suffered serious attack in the 1100°C cyclic and isothermal tests. The more severe cyclic test showed alloys LA1, LA2 and LA9 to be the best of the development brazes. The appearance of parent alloy porosity in the braze area after the cyclic test is a feature requiring further investigation.

SECTION 7

ADDENDUM

PREPARATION OF EXPERIMENTAL ALLOYS IN THE FORM OF FOIL

As previously reported it has been considered essential to produce the final selection of experimental braze alloys in the form of foil. This could then be used to produce porosity-free joints and then the mechanical properties of the alloys could be compared with each other and with competitive commercially available materials.

Preliminary experiments, reported in Phase 4 indicated that melt spinning onto a water cooled wheel could give metal ribbon from the trial compositions. However, the equipment available for use in the UK, at Sheffield and Cambridge Universities, either did not have the necessary protective environment or could not produce the required width of ribbon which was 5 mm minimum.

Therefore Allied Chemicals in New Jersey, who manufacture commercial quantities of metal foil, undertook to run trials with our alloys. The additional cost of this work, \$5000, was underwritten by AFML. At the time of writing this final summary report only limited success has been achieved by Allied Chemicals but it is reported as follows so that the sponsors can comment at the final review meeting.

Following on from the end of Phase 4 the alloys listed below were prepared as 4 X 50 gm argon arc melted button and submitted to Allied Chemicals.

	Cr	Ni	Pd	W	Mo	Si	Al
1A-9	44	32	10	5	5	2	2
1A-2	44	40	10	10	-	-	-
1A-3	44	40	11	5	-	-	-
1A-5	44	42	12	-	-	2	-
1A-1	44	40	11	5	-	-	-
TD-6	22	52	-	5	17	4	-
TD-20	16	50	-	5	25	4	-

The reported results obtained on all these alloys except 1A-5 were as follows:-

<u>Alloy No.</u>	<u>Comments</u>
1A-9	Brittle, poor run, some short ribbon made at 1250°C. Half of the alloy did not flow through the tube.
1A-9	Brittle, better control, casting temperature 1250°C. Burnt ribbon with holes made.
1A-2	Somewhat ductile, broken ribbons, started to flow through crucible at 1300°C. Some burnt pieces made.
1A-2	Burnt, somewhat ductile ribbon made.
1A-3	Broken ductile ribbon made. Started to flow through the crucible at 1200°C.
TD-6	Would not flow through the crucible.
TD-6	Same as above.
TD-20	Would not flow through the crucible.
TD-20	Same as above.
1A-1	Burnt, somewhat ductile ribbons made. Started to flow through the crucible at about 1250°C.
1A-1	Same as above.

In view of these discouraging results which indicated a lack of the fluidity needed to produce a good ribbon an addition of about 3% boron was made to 1A-5. This was done in the light of Allied's experience on foil preparation and enabled a reasonable foil with 6 mm width to be produced.

The analysed composition of this material, after melting was

40.39	Ni
42.30	Cr
11.54	Pd
2.40	Si
3.37	B

The melting point, determined by DTA, of 1A-5 before adding boron was 1235°C and of the alloy above 1200°C.

The obvious drawbacks to this material are firstly that its melting point is on the low side and secondly, in the light of

results in Phase 2 the boron may give problems with oxidation resistance. However, the above composition may not represent the optimum balance between melt flow properties and braze characteristics but, before any further work is done on varying the composition, trials will be made to determine if the ribbon obtained so far can be used to produce porosity free joints.

SECTION 8

CONCLUSIONS

- (1) From the 60 ternary bases investigated as potential brazes for INCOLOY alloy MA956 the following have been rejected for the reasons given:-
 - a) alloys in the Fe-Cr-Si system because of poor flow properties and ease of cracking.
 - b) alloys in the Fe-Cr-Ge system because of either low melting points ($\leq 1150^{\circ}\text{C}$), poor flow properties or ease of cracking.
 - c) alloys in the Fe-Cr-B system because of lack of oxidation resistance at 1100°C .
 - d) alloys in the Fe-Cr-Pd system because of either poor flow properties or unacceptable rates of oxidation.
 - e) alloys in the Ni-Cr-Ge system because of either unacceptable porosity in the braze, poor stress rupture properties or low oxidation resistance.
- (2) From the alloys in the Ni-Cr-Pd system the one selected as the most promising braze in terms of its brazing properties, cost, strength at 1100°C and corrosion resistance is 44 Ni-44 Cr-12 Pd.
- (3) Trials on the 44 Ni-44 Cr-12 Pd base alloyed with tungsten, molybdenum, aluminium and/or silicon produced materials which had melting points above 1200°C and acceptable brazing characteristics.
- (4) A meaningful comparison of high temperature mechanical properties of these alloys was not possible using joints made with powders or turnings since variable and sometimes large amounts of porosity was present in the brazes. Before this aspect of the work can be pursued it will be necessary to prepare the alloys in foil form so that they can be preplaced for joint preparation and hopefully produce sound brazes.
- (5) Static and cyclic oxidation tests at 1100°C on joints made with alloys from (3) above showed that the ones containing tungsten (5-10%) had the best properties which compared well with those obtained from commercial alloys.

SECTION 9

RECOMMENDATIONS

The main aim of any future work must be:-

- 1) To prepare the potential braze alloys in the form of foil.
- 2) To determine if, by using pre-placed foils, porosity free joints can be consistently obtained.

If this objective is not achieved it may be worthwhile trying pre-treatment of the MA956 surface to improve wettability e.g.

Ni-plating
de-aluminising
chemical etching

Once porosity free joints have been obtained comparison of the mechanical properties of the quaternary alloys can be made.

If, as is suggested by first results from Allied Chemicals on foil preparation, it is necessary to modify the compositions of the experimental braze alloys to make foils then the effect of these modifications on brazing properties and oxidation resistance must be assessed. In particular, it was shown in Phase 1, boron containing alloys do not have good oxidation resistance but it may be possible to overcome this problem by a pre-service diffusion treatment in vacuum.

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TABLE 1

NOMINAL COMPOSITIONS OF INCOLOY ALLOY MA956
AND TWO BRAZE ALLOYS DEVELOPED FOR DISPERSION STRENGTHENED NICKEL BASE ALLOYS

	Fe	Cr	Al	Ti	Y ₂ O ₃	Ni	Mo	Si	W
Alloy MA956	Bal	20	4.6	0.5	0.5	-	-	-	-
TD6	-	22	-	-	-	Bal	17	4	5
TD20	-	16	-	-	-	Bal	25	4	5

TABLE 2
COMPARISON OF NI-X AND FE-X
ALLOY SYSTEMS (DATA FROM REF.1)

Ni-base System	System Type	% X	Melting Point (°C)	Fe-base System	System Type	% X	Melting Point (°C)
Ni-Cr	Eutectic	51	1345	Fe-Cr	Congruent Melting	20	1507
Ni-Pd	Congruent Melting	60	1237	Fe-Pd	Congruent Melting	65	1310
Ni-Ge	Eutectic	34	1135	Fe-Ge	Eutectic	34.5	1125
Ni-Si	Eutectic	11.5	1125	Fe-Si	Eutectic	20.5	1200
Ni-B	Eutectic	4	1140	Fe-B	Eutectic	3.8	1149

TABLE 3
RESULTS OF INITIAL SCREENING TESTS ON 60 EXPERIMENTAL ALLOYS

BRAZE ALLOY	COMPOSITION (wt %)				MELTING PT. (BY D.T.A.) °C	BRAZE TEMP. °C	BRAZE VACUUM (mm Hg)	SPREAD	TEE-FILLET FLOW	CONTACT ANGLE	QUALITY		
	Ni	Cr	Pd								LARGE PORES	SMALL PORES	EROSION
1A	44.2	44.0	11.8		1305	1320	6 x 10 ⁻⁵	Good	Good	10°	1	1	2
2A	45.6	25.1	29.2		1260	1320	"	"	"	20	2	0	2
3A	11.2	35.2	53.6		1260	1280	"	V.Good	V.Good	3	1	0	1
4A	51.0	26.5	22.5		1287	1340	"	"	"	20	2	1	3
5A	38.3	41.2	20.5		1260	1300	8 x 10 ⁻⁵	Good	Good	10	2	0	1
6A	32.2	36.5	31.3		1242	1265	6 x 10 ⁻⁵	"	"	20	1	1	1
7A	27.6	31.6	40.8		1242	1265	"	"	"	10	2	0	1
8A	32.5	20.0	47.5		1250	1275	7 x 10 ⁻⁵	V.Good	V.Good	20	1	0	1
9A	18.6	35.6	45.8		1250	1275	"	"	"	20	2	1	2
10A	52.8	30.4	16.8		1305	1340	9 x 10 ⁻⁵	"	"	10	1	1	1
1B	59.7	35.4	4.9	Ge	1345	1370	3 x 10 ⁻⁵	V.Good	V.Good	20	1	1	2
2B	39.9	50.4	9.7		1365	1385	8 x 10 ⁻⁵	Reasonable	Good. Uneven Fillet	15	1	1	2
3B	65.9	19.4	14.7		1295	1320	6 x 10 ⁻⁵	V.Good	Good	10	1	2	2
4B	64.2	31.0	4.8		1315	1375	4 x 10 ⁻⁵	Good	Good. Uneven Fillet	25	2	1	1
5B	54.8	40.2	5.0		1306	1340	5 x 10 ⁻⁵	"	Good. Tapering Fillet	15	1	1	1
6B	65.4	25.0	9.6		1295	1340	9 x 10 ⁻⁵	Reasonable	Reasonable	10	1	2	1
7B	60.0	30.0	10.0		1250	1315	6 x 10 ⁻⁵	"	Good. Tapering Fillet	10	2	2	1
8B	49.9	40.2	9.9		1260	1315	"	"	"	15	1	2	1
9B	60.1	25.0	14.9		1305	1325	3 x 10 ⁻⁵	"	" Small Back Fillet	25	2	2	2
10B	55.1	29.5	15.4		1250	1290	7 x 10 ⁻⁵	Good	Good	15	1	1	2
1C	72.7	20.1	7.2	Si	1390	1410	5 x 10 ⁻⁵	V.Little	Reasonable. V.Small Fillet	30	2	1	0
2C	76.4	10.0	13.6		1250	1270	8 x 10 ⁻⁵	None	None	45	0	0	0
3C	70.3	9.7	20.0		1170	1220	7 x 10 ⁻⁵	"	"	90	Did not adhere to substrate		
4C	77.0	15.4	7.6		1435	1460	6 x 10 ⁻⁵	V.Little	"	25	1	1	0
5C	71.8	15.0	13.2		1250	1270	8 x 10 ⁻⁵	None	"	45	0	0	0
6C	65.2	14.7	20.1		1170	1220	7 x 10 ⁻⁵	"	"	90	As 3C above		
7C	66.9	19.7	13.4		1250	1270	8 x 10 ⁻⁵	"	"	45	0	0	0
8C	60.2	19.9	19.9		1200	1230	4 x 10 ⁻⁵	"	"	90	As 3C above		
9C	82.8	10.1	7.1		1390	1410	5 x 10 ⁻⁵	V.Little	Reasonable. V.Small Fillet	40	1	1	0
10C	80.0	10.1	9.9		1400	1420	6 x 10 ⁻⁵	Reasonable	"	25	1	1	0

Continued

TABLE 3 (Continued)

BRAZE ALLOY	COMPOSITION (wt %)			MELTING PT. (BY D.T.A.)	BRAZE TEMP. °C	BRAZE VACUUM (mm Hg)	SPREAD	TEE-FILLET FLOW	CONTACT ANGLE	QUALITY		
	Fe	Cr	Ge							LARGE PORES	SMALL PORES	EROSION
1D	58.4	21.6	20.0	1365	1385	5 x 10 ⁻⁵	Reasonable	Uneven	10°	0	0	0
2D	60.6	15.7	23.7	1275	1325	8 x 10 ⁻⁵	V. Little	Reasonable. Small Fillet	25	1	0	0
3D	55.5	20.0	24.5	1275	1325	"	"	"	20	0	0	0
4D	49.4	25.2	25.4	1450	"	5 x 10 ⁻⁵	None	None	-	-	-	-
5D	50.8	14.9	34.3	1103	1125	"	"	"	90	0	0	2
6D	46.4	19.2	34.4	1103	"	"	"	"	100	0	0	1
7D	41.0	24.0	35.0	1103	"	"	"	"	100	0	0	2
8D	53.6	30.2	15.2	1440	1460	6 x 10 ⁻⁵	"	"	20	2	2	0
9D	35.2	20.1	44.7	1103	1145	"	Reasonable	Reasonable. Small Fillet	50	2	1	3
10D	24.8	18.2	57.0	1055	1075	7 x 10 ⁻⁵	Good	V. Little	10	2	1	1
1E	45.3	15.0	39.7	1348	1375	7 x 10 ⁻⁵	V. Good	V. Good	10	0	0	1
2E	40.4	20.4	39.2	1320	1340	"	"	"	5	0	0	0
3E	35.1	25.1	39.8	1320	1340	"	"	"	20	1	0	1
4E	26.0	15.4	58.6	1340	1365	5 x 10 ⁻⁵	"	"	10	0	1	0
5E	21.0	19.9	59.1	1330	1350	4 x 10 ⁻⁵	Good	Good	10	0	1	2
6E	15.1	25.1	59.8	1320	1340	8 x 10 ⁻⁵	V. Good	V. Good	20	1	2	1
7E	30.3	20.4	49.3	1320	1340	"	"	Reasonable	10	1	0	1
8E	14.7	35.1	50.2	1312	1320	6 x 10 ⁻⁵	"	V. Good	10	1	2	1
9E	50.2	20.6	29.2	1347	1370	"	"	"	5	0	1	1
10E	34.3	35.3	30.4	1320	1410	5 x 10 ⁻⁵	Good	"	10	1	1	1
1F	83.1	14.9	2.0	1228	1260	6 x 10 ⁻⁵	Reasonable	Good. Uneven Fillet	10	0	0	0
2F	82.0	14.9	3.1	1250	1270	4 x 10 ⁻⁵	V. Good	V. Good	5	0	0	0
3F	77.2	19.8	3.0	1242	1290	7 x 10 ⁻⁵	"	Good. Small Back Fillet	5	0	0	0
4F	72.0	25.0	3.0	1218	1240	3 x 10 ⁻⁵	None	None	10	1	1	0
5F	78.2	19.8	2.0	1235	1260	6 x 10 ⁻⁵	Reasonable	Good	10	0	0	1
6F	81.6	14.7	3.7	1260	1290	7 x 10 ⁻⁵	V. Good	V. Good	10	1	0	0
7F	77.0	19.5	3.5	1210	1240	5 x 10 ⁻⁵	None	None	90	0	0	1
8F	71.1	25.0	3.9	1218	1250	6 x 10 ⁻⁵	"	"	135	0	0	0
9F	73.2	24.9	1.9	1242	1260	6 x 10 ⁻⁵	"	"	15	0	1	0
10F	86.8	10.0	3.2	1200	1225	8 x 10 ⁻⁵	V. Little	Good	25	0	1	0
TD6 W1 - 22 Cr - 17 Mo - 4 Si - 5W					1300	4 x 10 ⁻⁵	Good	Good	10	2	1	2
TD20 W1 - 16 Cr - 25 Mo - 4 Si - 5W					1300	"	"	Uneven Fillet	20	2	1	2

TABLE 4
ALLOYS SELECTED FOR FURTHER EVALUATION
IN PHASE 2

ALLOY NO.	COMPOSITION					BRAZE TEMP °C
1A	44.2 Ni	44.0 Cr	11.8 Pd			1320
6A	32.2 Ni	36.5 Cr	31.3 Pd			1265
8A	32.5 Ni	20.0 Cr	47.5 Pd			1275
1B	59.7 Ni	35.4 Cr	4.9 Ge			1370
5B	54.8 Ni	40.2 Cr	5.0 Ge			1340
2E	35.1 Fe	25.1 Cr	39.8 Pd			1340
4E	40.4 Fe	20.4 Cr	39.2 Pd			1365
9E	50.2 Fe	20.6 Cr	29.2 Pd			1370
3F	73.2 Fe	24.9 Cr	1.9 B			1290
5F	77.2 Fe	19.8 Cr	3.0 B			1260
6F	72.0 Fe	25.0 Cr	3.0 B			1290
TD6	22 Cr	17 Mo	4 Si	5W	Ni Bal	1300
TD20	16 Cr	25 Mo	4 Si	5W	Ni Bal	1300

TABLE 5
TENSILE TESTS 1100°C

Spec.	% Pores	Shear Stress		Failure* Mode
1A-A	10	2254 psi	15.5 N/mm ²	P-S
1A-B	5	2254	15.5	P-T
6A-B	2	2666	18.4	P-S
6A-D	10	2666	18.4	P-S
8A-G	5	2156	14.9	P/B
5B-F	0	3030	20.8	P/B
5B-H	40	1905	13.1	P-T
4E-A	3	2458	17.2	P-T
4E-B	5	3141	21.6	P-T
2E-A	0	3121	21.5	P-T
2E-B	0	3255	22.5	P-S
9E-C	10	2475	17.1	P-T
3F-G		2411	16.6	P-T
3F-K	15	2642	18.3	P/B
6F-G	10	3347	23.0	P-T
6F-J	3	2884	19.8	P-T
5F-G	5	3174	21.9	P-T
5F-H	5	3391	23.3	P-T
TD6-A	50	2594	17.9	P/B
TD6-C	50	1271	8.8	P-T
TD20-A	50	2538	17.5	P-T
TD20-B	50	2120	14.6	P-S

* P-S Shear failure in parent (MA956) sheet parallel to braze

P-T Failure in parent sheet transverse to stress direction

P/B Failure at parent sheet/braze interface

TABLE 6
STRESS RUPTURE TESTS 1100°C

Spec.	% Pores	Shear Stress on Braze	Life hrs	Failure* Mode
1A-C	0	4.6 N/mm ²	120.6	B
6A-A	15	5.1	190.4	-
6A-H		5.1	106.2	P-T
8A-D	30	4.6	87.8	P-T
8A-H	30	5.6	28.0	P-T
1B-G	20	7.5	0.2	P-T
1B-H	10	5.4	2.4	B
1B-J	30	5.1	1.4	P-T
5B-G	30	5.7	1.0	P-T
5B-K	40	4.8	2.1	P-T
2E-E	0	4.2	85.0	P-T
2E-D	0	5.0	29.9	B
4E-E	5	3.9	35.6	P-T
4E-F	5	4.5	29.5	B
4E-D	10	3.6	162.4	B
9E-A	2	4.6	30.5	B
9E-D	0	5.3	41.8	P-T
3F-H	0	4.9	6.0	B
3F-J	0	5.1	17.8	B
5F-J	0	4.9	1.7	P-T
5F-K	5	5.7	1.4	P-T
6F-H	10	4.8	2.8	P-T
6F-K	5	4.8	1.4	P-T
TD6-B	50	7.7	0.2	B
-D	50	5.6	1.0	B
TD20-C	50	4.8	0.3	P-T
-D	50	4.8	0.2	B

- * P-S Shear failing in parent (MA956) sheet parallel to braze
- P-T Failure in parent sheet transverse to stress direction
- P-B Failure at parent sheet/braze interface
- B Failure within braze metal

TABLE 7
RESULTS OF ISOTHERMAL OXIDATION EXPOSURE
FOR 1000hr/1100°C IN AIR

<u>Sample</u>	<u>Comp.</u>	<u>Approx. depth of oxide penetration</u>
1A	44Ni-44Cr-12Pd	3 μ thick continuous oxide on surface
6A	32Ni-37Cr-31Pd	60 μ becoming discontinuous as depth increases
8A	32Ni-20Cr-48Pd	Complete penetration following 2 phase dendritic structure
1B	60Ni-35Cr-5Ge	Solid oxide on surface up to 30 μ thick in patches
5B	55Ni-40Cr-5Ge	Penetration throughout structure
2E	35Fe-25Cr-40Pd	Patches of solid oxide up to 30 μ deep plus discontinuous oxide to same depth
4E	40Fe-20Cr-40Pd	Patches of solid oxide up to 60 μ deep plus discontinuous oxide to same depth
9E	50Fe-20Cr-30Pd	Patches of solid oxide up to 60 μ deep plus discontinuous penetration to 120 μ
TD6*	Ni-22Cr-17Mo-4Si-5W	Coarse, discontinuous, oxides to 150 μ depth
TD20*	Ni-16Cr-25Mo-4Si-5W	Patches of solid oxide to 70 μ depth plus patches of discontinuous to 30 μ

* Commercial alloys

TABLE 8
RESULTS OF CYCLIC OXIDATION TESTS IN AIR (1100°C-R.T.)

Sample	Composition	Approx. depth of Oxidation
1A	44Ni-44Cr-12Pd	Adherent scale. Interdendritic oxide penetrations to 0.12mm.
6A	32Ni-37Cr-31Pd	Adherent scale. Internal pores to 0.3mm below 0.05mm external oxide.
8A	32Ni-20Cr-48Pd	Adherent scale. Thicker surface oxide layer (0.1mm) than 1A & 6A.
1B	60Ni-35Cr-5Ge	Reasonably adherent scale. Oxide penetration to 0.2mm.
5B	55Ni-40Cr-5Ge	Reasonably adherent scale. Oxide penetration to 0.2mm.
2E	35Fe-25Cr-40Pd	Very loose oxide scale 0.2mm thick.
4E	40Fe-20Cr-40Pd	Loss in sample thickness of 0.8mm + loose external oxide 0.35mm thick.
9E	50Fe-20Cr-30Pd	Loss in sample thickness of 0.6mm + loose external oxide 0.1mm thick.
3F	75Fe-25Cr-2B	Completely oxidised.
5F	77Fe-20Cr-3B	Completely oxidised.
6Fq	72Fe-25Cr-3B	Completely oxidised.
TD6*	Ni-22Cr-17Mo-4Si-5W	Thin adherent scale + discontinuous oxide to 0.1mm
TD20*	Ni-16Cr-25Mo-4Si-5W	As TD6 but oxide to 0.15mm

*Commercial alloys

Tests carried out for 312h, except for alloys 3F, 5F and 6F which were curtailed at 24h.

TABLE 9
ANALYSIS OF BRAZES EXAMINED IN PHASES 3 & 4

Alloy	Ni	Fe	Cr	Pd	W	Mo	Al	Si
1A-1	40.6		44.7	10.0	4.7			
2	36.7		44.7	8.7	9.6			
3	40.6		44.7	9.8		4.9		
4	36.5		44.6	8.9		10.0		
5	42.5		44.6	10.9				2.0
6	35.0		44.4	8.8	4.7	5.1		2.0
7	42.8		44.8	10.9			1.5	
8	41.3		45.4	9.9			3.3	
9	33.1		45.6	8.1	5.2	5.2	1.5	1.3
8E-1		13.4	36.1	40.2	10.4			
2		13.1	35.5	41.2		10.2		
3		15.7	36.5	46.7				1.1
4		14.7	36.5	46.5			2.3	
5		12.6	36.5	38.1	5.3	5.3	1.1	1.1

TABLE 10
BRAZING PROPERTIES OF PHASE 3 ALLOYS

Brazing Alloy	Melting Point by DTA, °C	Brazing Temp., °C	Brazing Vacuum mm Hg	Spread	T-Fillet Flow	Contact Angle	QUALITY			Comments
							Large Pores	Small Pores	Erosion	
1A	1305	1320	6x10 ⁻⁵	Good	Good	10°	1	1	2	
1A-1	1305	1340	4x10 ⁻⁵	V. Good	V. Good	10°	2	1	1	
1A-2	1285	1350	4x10 ⁻⁵	V. Good	V. Good	20°	1	0	0	
1A-3	1295	1325	7x10 ⁻⁵	V. Good	V. Good	10°	1	1	1	
1A-4	1295	1375	8x10 ⁻⁵	Reasonable	Good. Small Back Fillet	20°	2	1	2	(Cracked)
1A-5	1235	1350	6x10 ⁻⁵	V. Good	V. Good	20°	2	1	2	
1A-6	1235	1360	8x10 ⁻⁵	Reasonable	Good. Small Fillets	10°	2	1	1	
1A-7	1295	1320	5x10 ⁻⁵	Good	Good. Small Fillets	10°	2	1	1	
1A-8	1275	1320	5x10 ⁻⁵	Reasonable	Reasonable	15°	0	2	0	
1A-9		1360	5x10 ⁻⁵	Reasonable	Good. Small Fillets	30°	1	1	1	
8E	1312	1320	6x10 ⁻⁵	V. Good	V. Good	10°	1	2	1	
8E-1	1312	1400	8x10 ⁻⁵	Good	Good	20°	2	1	1	
8E-2		1400	7x10 ⁻⁵	Good	Good	20°				
8E-3	1242	1320	6x10 ⁻⁵	V. Good	V. Good	10°	0	0	1	
8E-4	1440(?)	1400	4x10 ⁻⁵	Reasonable	Poor	10°	2	1	0	(No adhesion)
8E-5	1140(?)	1400	5x10 ⁻⁵	Not completely molten						

TABLE 11
RESULTS OF 1000HR/1100°C/AIR EXPOSURE

Sample	Fig. No.	Depth of oxide penetration or porosity	Thickness of Surface Scale	Depth of dechromised layer	Remarks
1A-1	7	200 μ	20 μ	200 μ	Number of sub-surface oxide particles less than 1A-1.
1A-2	8	200 μ	Patchy	200 μ	
1A-3	9	200 μ	20 μ	200 μ	Discontinuous scale.
1A-4	10	200 μ	10-20 μ	nil	Isolated oxides to 400 μ depth.
1A-5	-	200 μ	20 μ Patchy	200 μ	
1A-6	-	300 μ Patchy	10 μ	nil	
1A-7	-	200 μ	Patchy	200 μ	Also fine filamentary oxide to 50 μ depth.
1A-8	-	800 μ	20 μ Patchy	100 μ	Also fine more copious oxide penetration to 100 μ .
1A-9	11	50 μ	10 μ	nil	Large & filamentary oxides at surface.
8E-1	12	200 μ	100 μ	200 μ	Thick scale contains metallic particles.
8E-2	13	20 μ	700 μ	nil	Metal particles in scale.
8E-3	(14 (15	50 μ	30 μ	80 μ	Severe metal erosion.
8E-4	16	10 μ	nil	nil	V. occasional sub-surface oxides.
8E-5	17	50 μ	20 μ	nil	

TABLE 12
STRESS RUPTURE RESULTS FROM
DOUBLE OVERLAP TEST PIECE (1100 °C)

Alloy	Overlap	Shear Stress ₂ on Braze N/mm ²	Life(hrs)	Failure Location
1A	Double	4.6	319	Braze
1A	Single	4.6	120.6	Braze
5B	Double	4.6	0.4	Braze
5B	Single	4.8	2.1	P-T*
2E	Double	4.6	70.2	Braze
2E	Single	5.0	29.9	Braze
3F	Double	4.6	0.07	Braze
3F	Single	4.9	6.0	Braze

Comparative results for single overlap specimens taken from phase 2.

*Failure in parent sheet transverse to stress direction.

TABLE 13
1100°C STRESS RUPTURE RESULTS

<u>Sample</u>	<u>% Porosity in joint</u>	<u>Stress (N/mm²)</u>	<u>Life (hrs)</u>
1A-3 (1)	6	3.0 to 408hr 4.0 to end	448.0
1A-3 (2)	16	3.0 to 404hr 4.0 to 500hr 6.0 to end	524.8
1A-5 (1)	4	3.0	39.9
1A-5 (2)	12	3.0	67.6
1A-5 (3)	16	3.0	11.5
1A-5 (4)	20	3.0	28.5
1A-9 (1)	17	3.0	9.4
1A-9 (2)	14	3.0	369.1

All samples failed in braze metal except 1A-5(1) which failed in the MA956 sheet adjacent to braze.

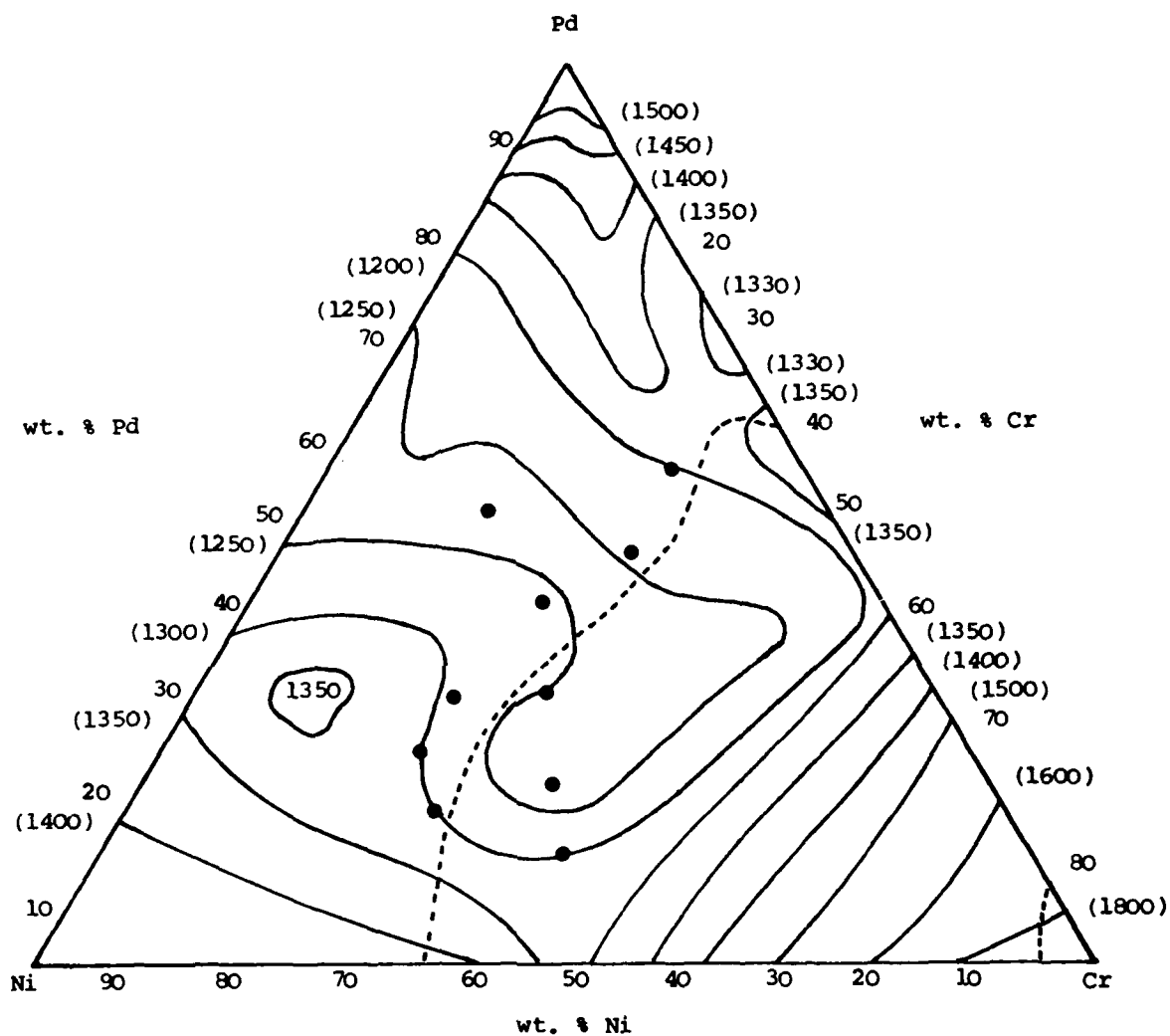


Figure 1 Ni-Cr-Pd System Liquidus isotherms plotted from data of Nemilov et al (Ref 2) and Rhys and Berry (Ref 6)
 Temperatures °C
 --- Approx. limit of solid solution
 ● Alloy compositions chosen for present work

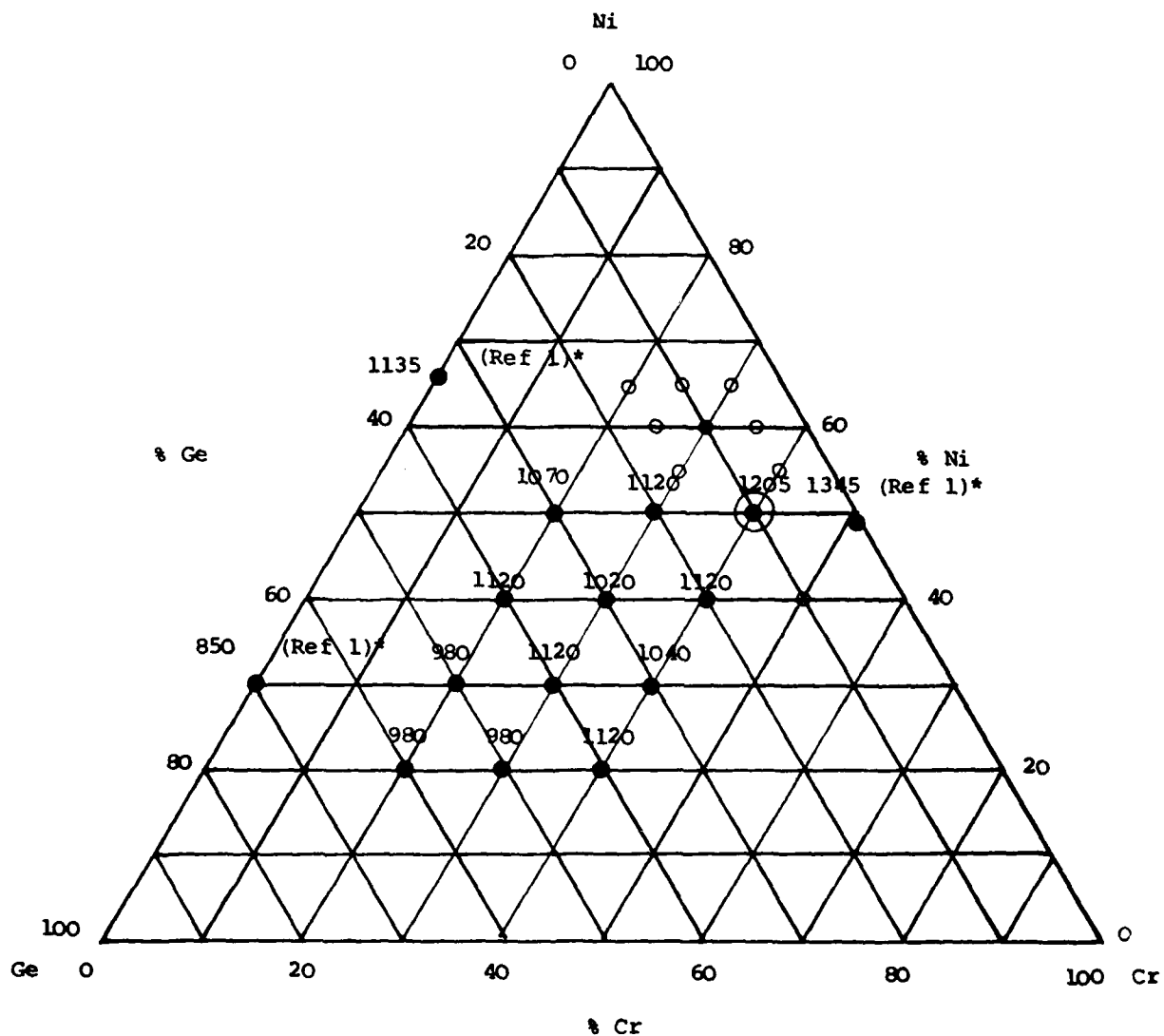


Figure 2 Approximate solidus data for the Ni-Cr-Ge system (derived from Ref 3). (* Liquidus). Temperature °C.

• Alloy compositions chosen for present work

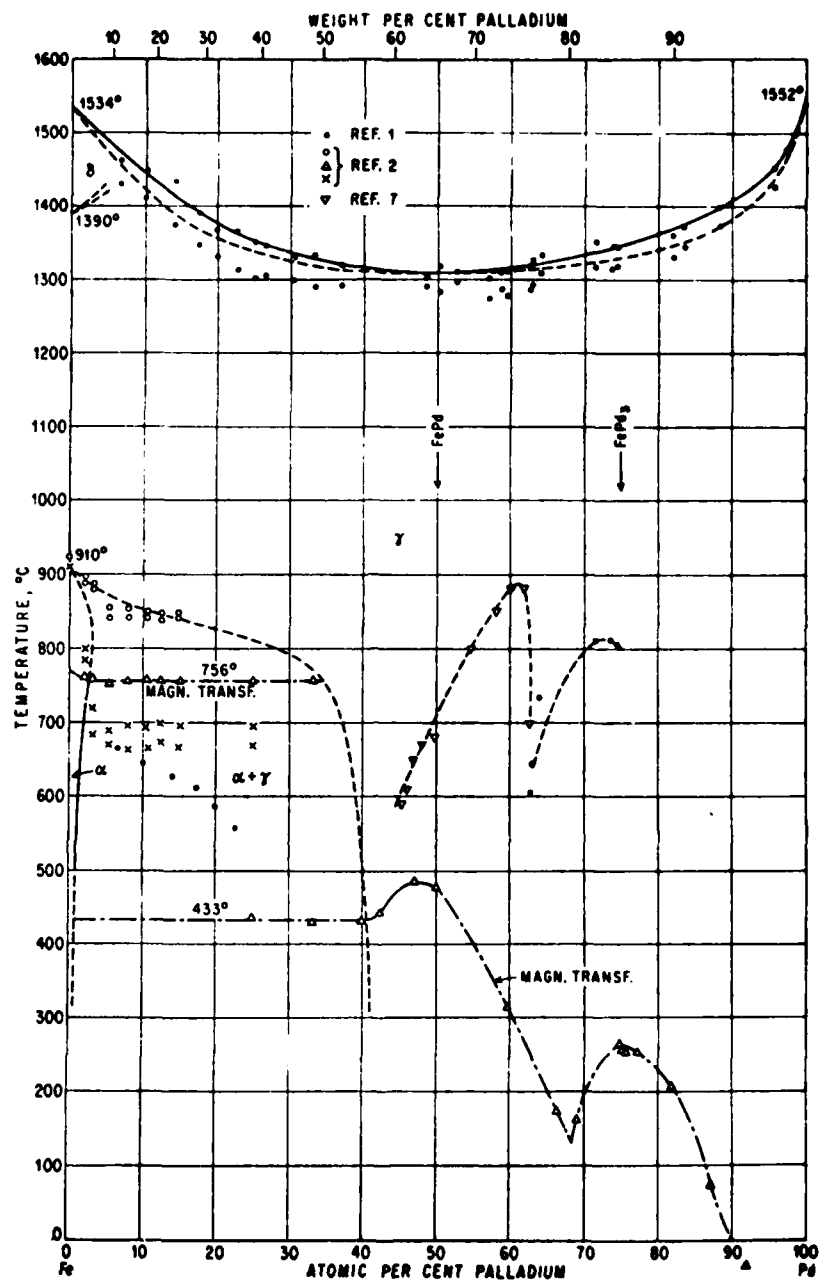


Figure 3 Fe-Pd (Ref. 1)

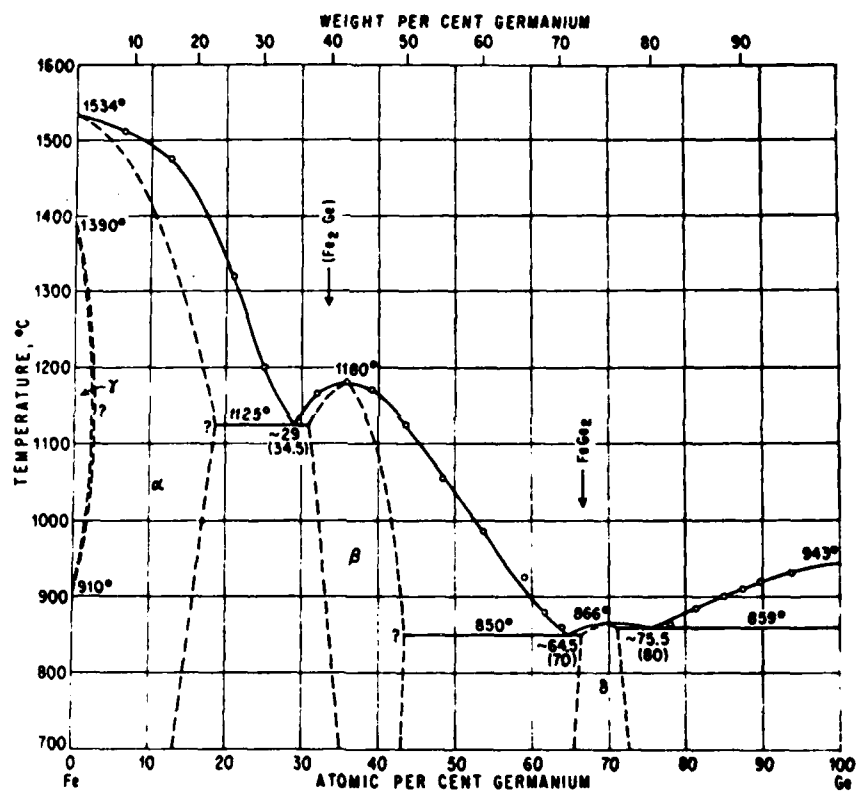


Figure 4 Fe-Ge (Ref. 1)

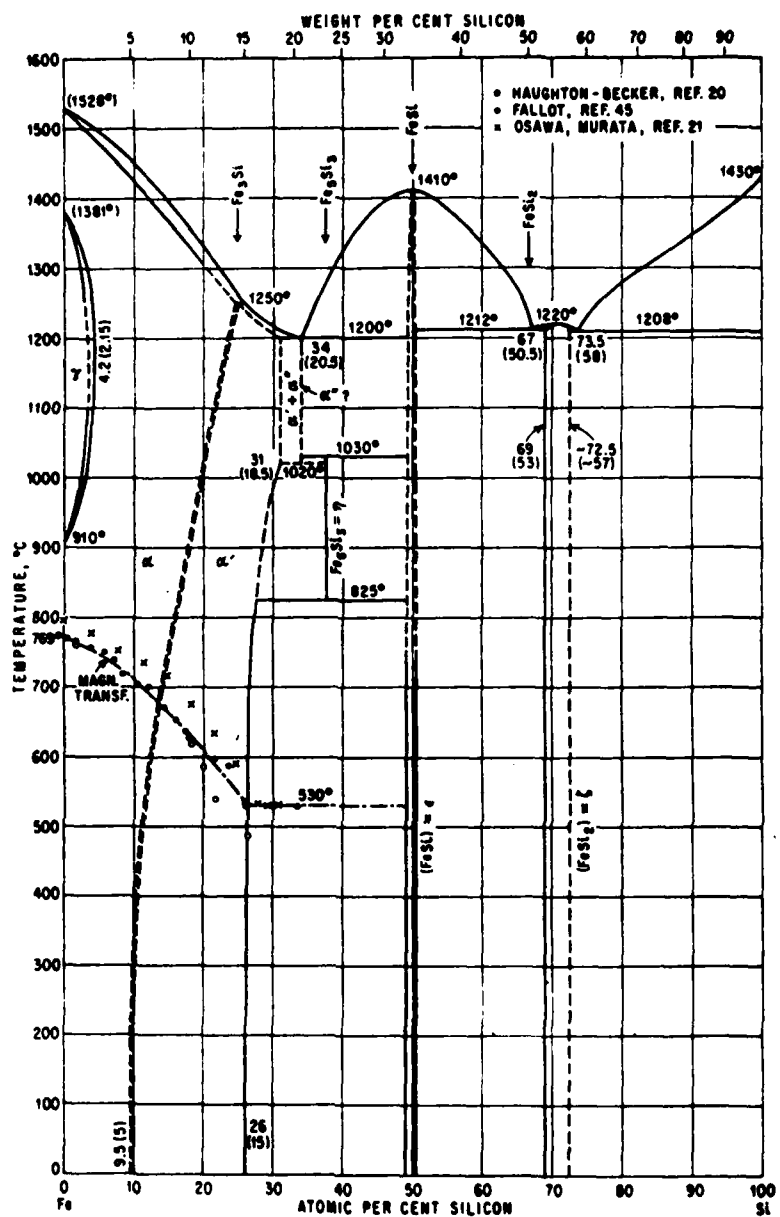
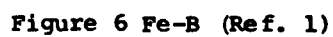


Figure 5 Fe-Si (Ref. 1)



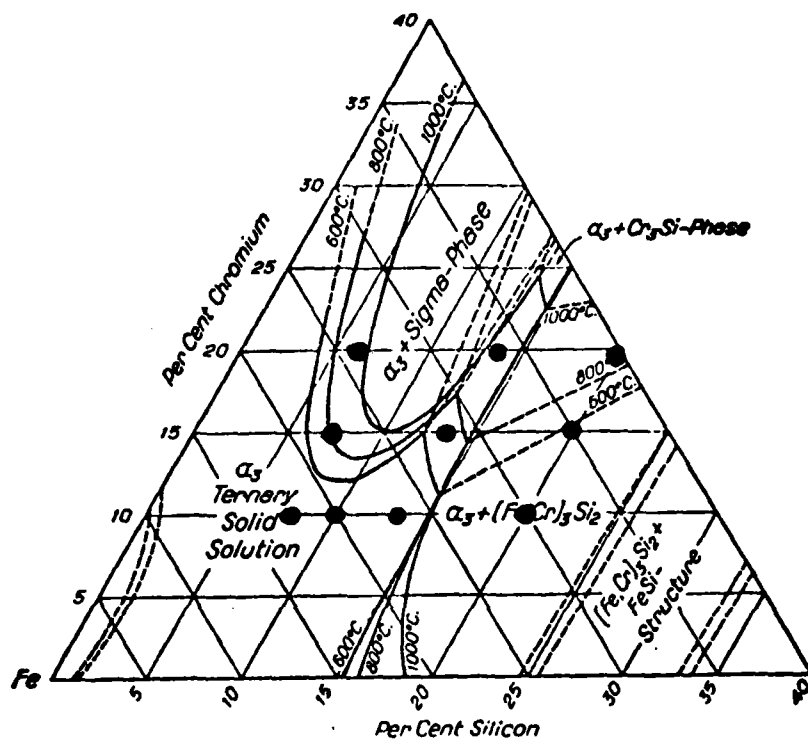


Figure 7 Fe-Cr-Si System. Constitutional diagram of the iron-rich solid solution range. Weight per cent. (Ref. 4)

● Alloy compositions chosen for present work

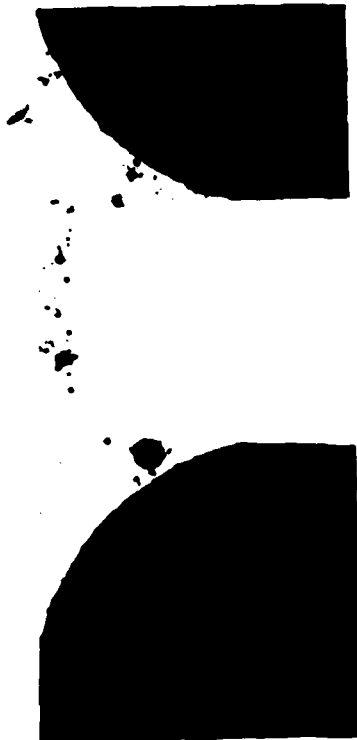


Fig. 8 (X26) B29961
T-braze with TD6 showing porosity.
(Unetched)

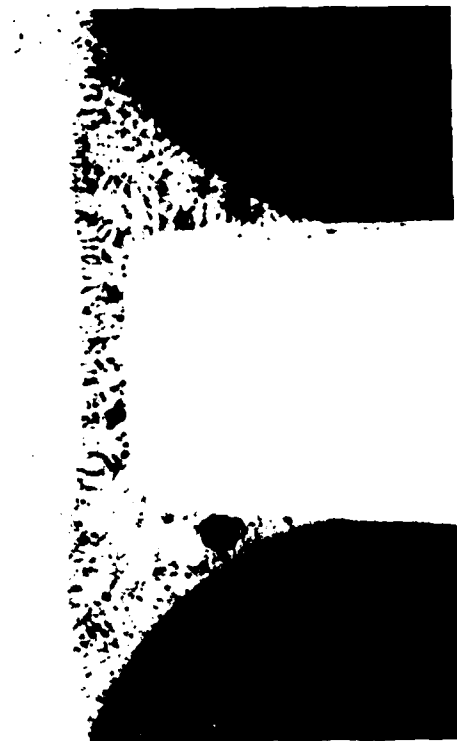


Fig. 9 (X31) B29978
As Figure 8 after etching.

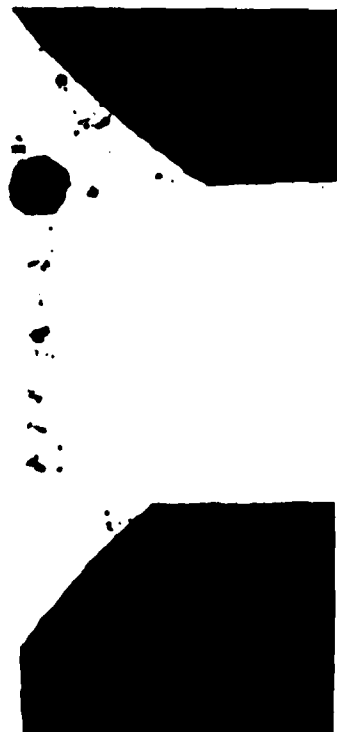


Fig. 10 (X31) B29958
TD20 Unetched.

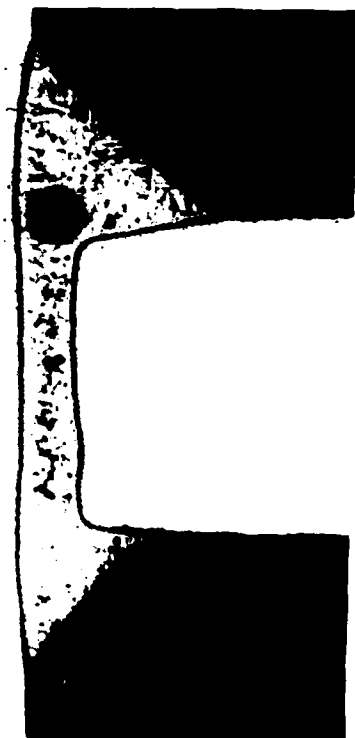


Fig. 11 (X31) B29980
As Figure 10 after etching.



Fig. 12 (X38) B29931
Unetched alloy 1A. Considered
acceptable.

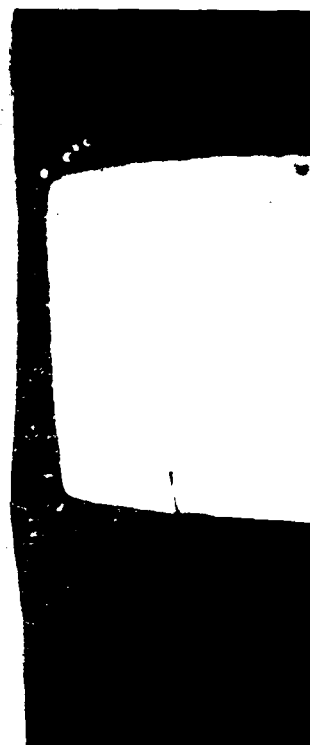


Fig. 13 (X37) B29962
As Figure 12 after etching.



Fig. 14 (X31) B29933
Unetched alloy 5A. Unacceptable
porosity.

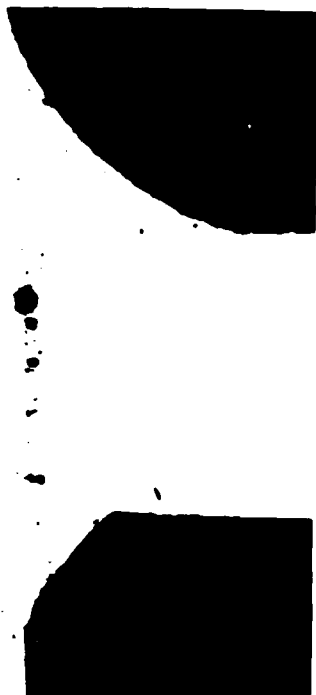


Fig. 15 (X31) B29939
Unetched Alloy 1B. Considered
acceptable.



Fig. 16 (X36) B29941
Unetched alloy 3B showing
unacceptable porosity.



Fig. 17 (X31) B30038
Alloy 7C. Rejected for non-
melting and cracking.

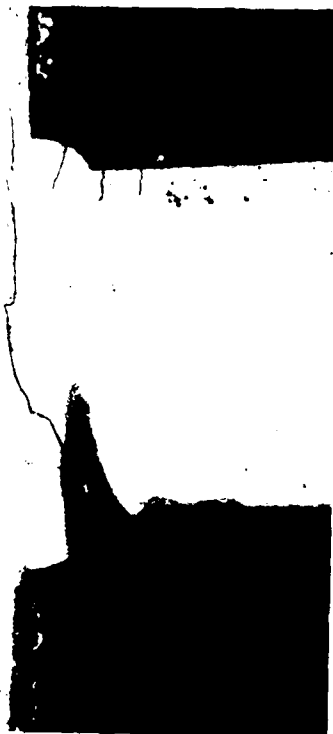


Fig. 18 (X40) B2990
Alloy 2D showing bad cracking in
braze extending into substrate.

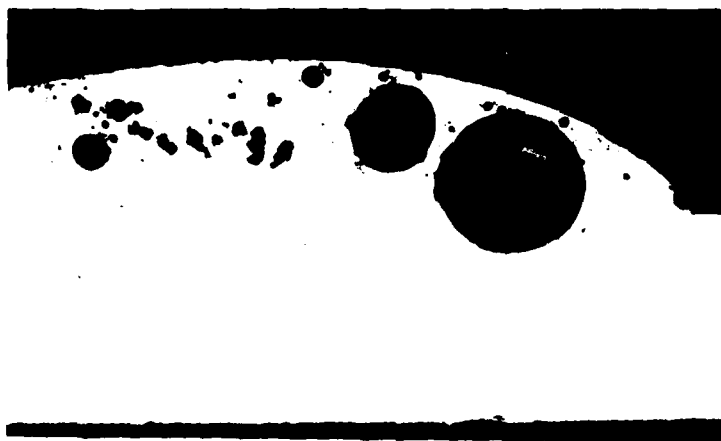


Fig. 19 (X20) B29948
Alloy 9D showing bad porosity and base metal erosion.

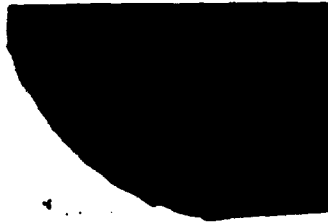


Fig. 20 (X25) B29951
Unetched alloy 9E. Considered acceptable.

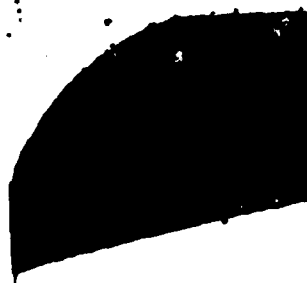


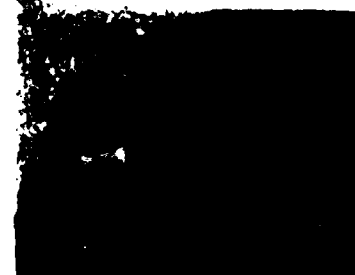
Fig. 21 (X31) B29973
Etched alloy 9E.



Fig. 22 (X31) B29954
Unetched alloy 5F. Considered acceptable.



Fig. 23 (X25) B29976
Etched alloy 5F.



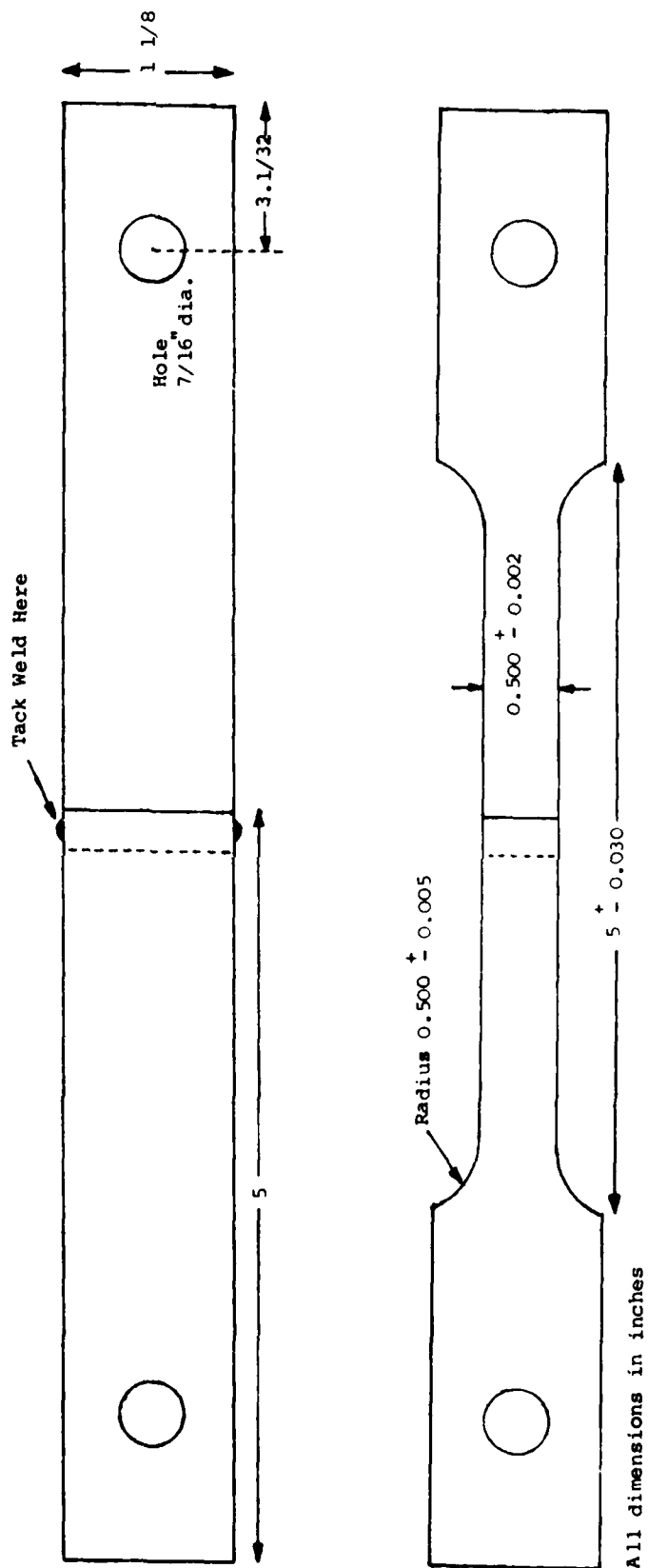


Figure 24. Dimensions of modified AWS lap-shear specimen



(a)



(b)

Fig. 25 X-ray pictures of brazes in mechanical test specimens showing
(a) Alloy 1A with no porosity (b) TD20 with 50% porosity (light areas).
Both pictures are about X3 from originals.

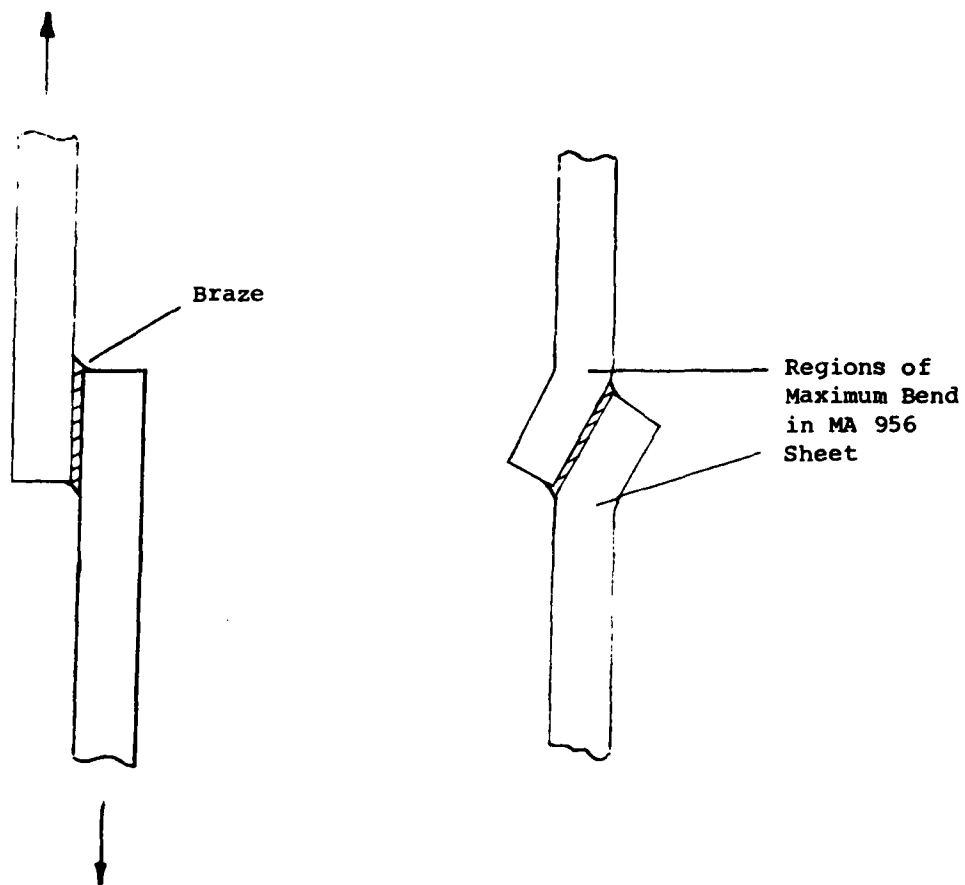


Figure 26 Section through AWS test piece before and after testing, showing how alignment of stress along test axis causes bending of MA 956 sheet at both ends of overlap. Failure thereby tends to occur in the 956 sheet rather than in the braze.



B38633

X31

Fig. 27 Shear fracture through MA956 in tensile test sample containing alloy 2E (35 Fe 25 Cr 40 Pd).



B30745

X27

Fig. 28 Transverse fracture through MA956 in tensile test sample containing alloy 3F (73 Fe 75 Cr 2 B).



B30744

X27

Fig. 29 Failure at MA956/braze interface in sample containing alloy 8A (32 Ni-20 Cr-48 Pd).



B30749

X27

Fig. 30 Failure within braze metal Alloy 4E (40 Fe-20 Cr- 40 Pd).



B30751

X27

Fig. 31 Alloy 6F (72 Fe-25 Cr- 3 B) showing attack of
MA956 sheet by volatile compound from braze.

Surface Appearance after Isothermal Exposure in air 1000h/1100°C



B30559 X100
Fig. 32 Alloy 1A (44 Ni-44 Cr- 12 Pd)



B30560 X520
Alloy 1A



B30548 X100
Fig. 33 Alloy 6A (32 Ni-37 Cr-31 Pd)



B30549 X520
Alloy 6A

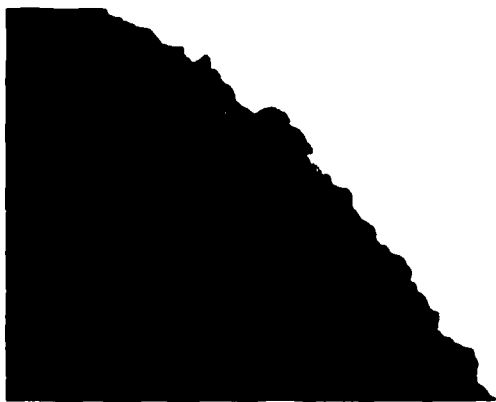


Fig. 34
Alloy 8A
(32 Ni-20 Cr-48 Pd)

B30558

X100

Surface Appearance after Isothermal Exposure in air 1000h/1100°C



B30554 X100
Fig. 35 Alloy 1B (60 Ni-35 Cr-5 Ge)



B30564 X520
Alloy 1B



B30557 X100
Fig. 36 Alloy 5B (55 Ni-40 Cr-5 Ge)



B30561 X250
Alloy 5B

Surface Appearance after Isothermal Exposure in air 1000h/1100°C



B30546 X100
Fig. 37 Alloy 2E (35 Fe 25 Cr 40 Pd)



B30547 X520
Alloy 2E



B30555 X100
Fig. 38 Alloy 4E (40 Fe 20 Cr 40 Pd)



Alloy 4E X520



B30552 X100
Fig. 39 Alloy 9E (50 Fe 20 Cr 30 Pd)



B30553 X520
Alloy 9E

Surface Appearance after Isothermal Exposure in air 1000h/1100°C



B30556
Fig. 40 Alloy TD6

X100



B30562
Alloy TD6

X520



B30550
Fig. 41 Alloy TD20

X100



B30551
Alloy TD20

X520

Surface Appearance after 312h Cyclic Oxidation in air (1100°C - R.T.)



Fig. 42 X200 VC2727
Alloy 1A (44 Ni-44 Cr-12 Pd)



Fig. 43 X200 VC2728
Alloy 6A (32 Ni-37 Cr-31 Pd)



Fig. 44 X200 VC2729
Alloy 8A (32 Ni-20 Cr-48 Pd)



Fig. 45 X200 VC2730
Alloy 1B (60 Ni-35 Cr-5 Ge)



Fig. 46 X200 VC2731
Alloy 5B (55 Ni-40 Cr-5 Ge)

Surface Appearance after 312h Cyclic Oxidation in air (1100°C - R.T.)



Fig. 47
Alloy 2E (35 Fe-25 Cr-40 Pd)

VC2732



Fig. 48
Alloy 4E (50 Fe-20 Cr-40 Pd)

VC2733

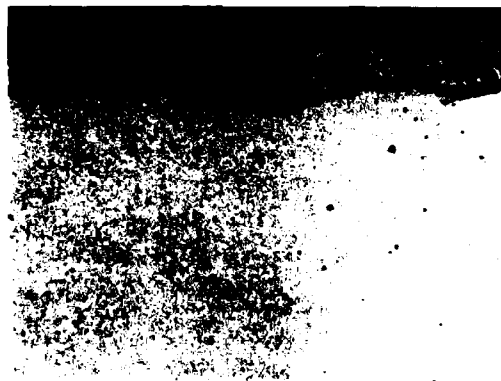


Fig. 49
Alloy 9E (50 Fe-20 Cr-30 Pd)

X200

VC2734



Fig. 50
Alloy TD6

X200

VC2725



Fig. 51
- 75 - Alloy TD20

X200

VC2726

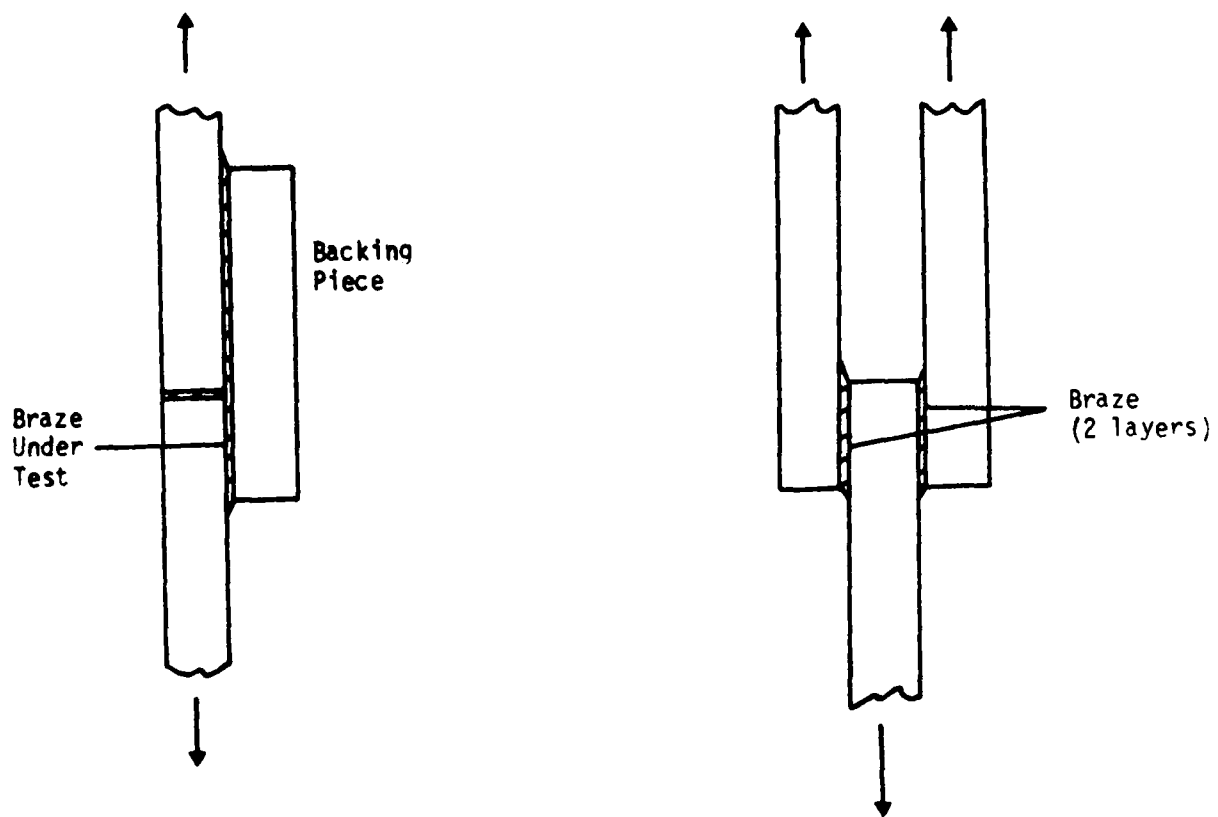
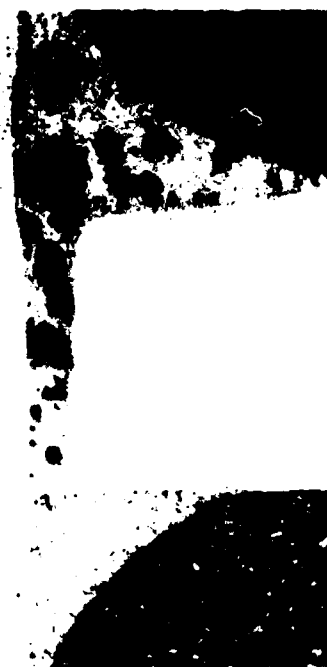


Figure 52 Possible alternative lap shear test pieces



X31

B31363

X31

(b)

B31369

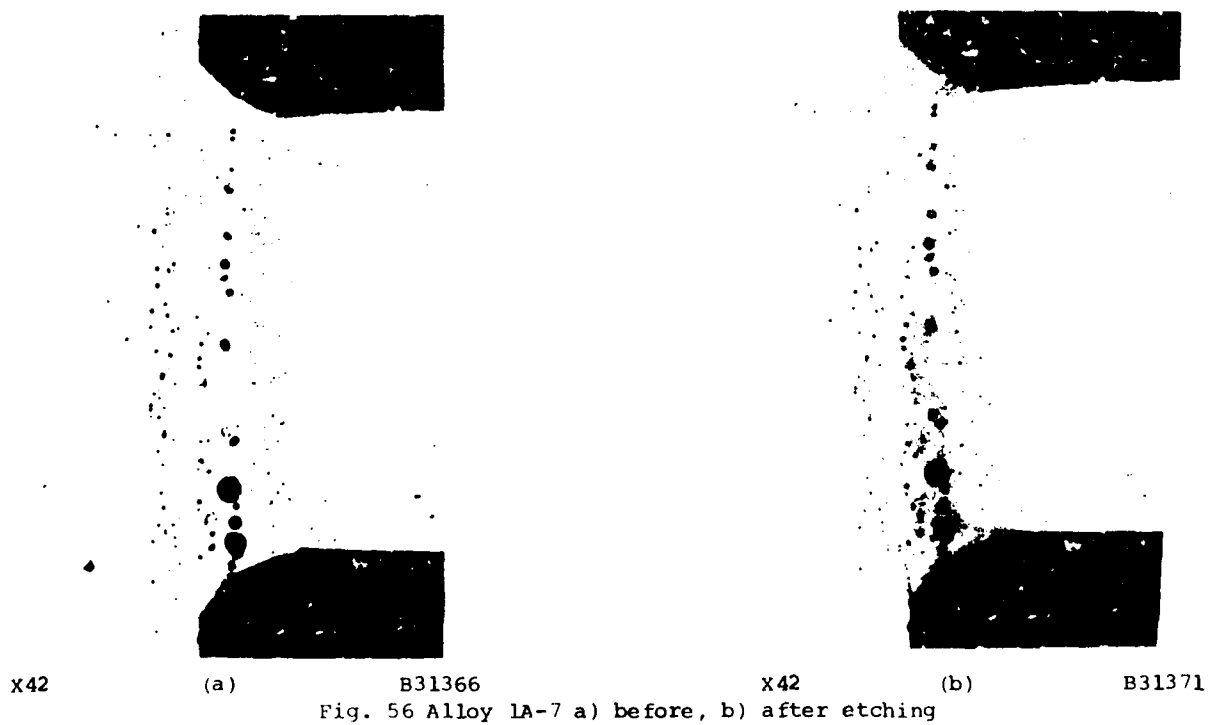
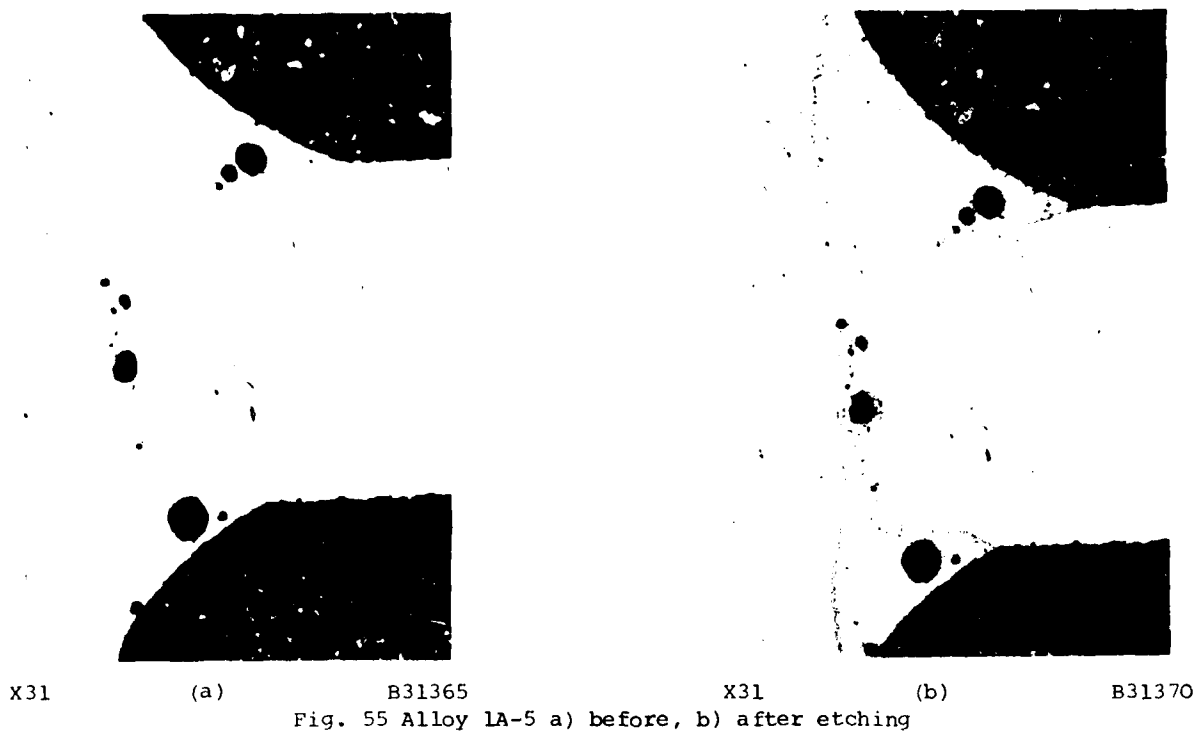
Fig. 53 Alloy 1A-1. T section braze a) before, b) after etching.

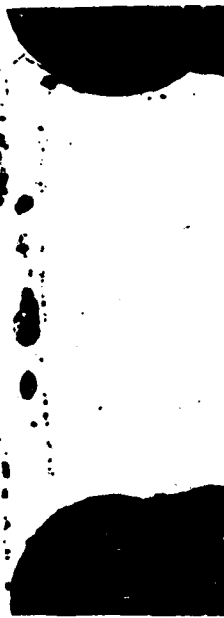


X31

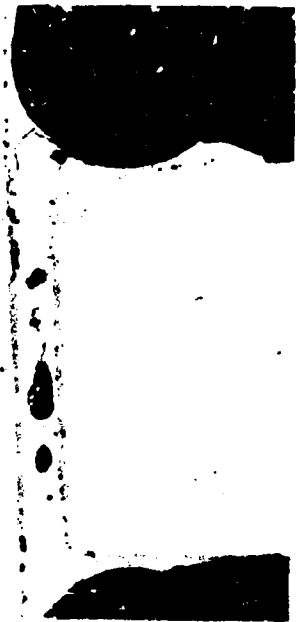
B31364

Fig. 54 Alloy 1A-4. Showing cracking in braze.

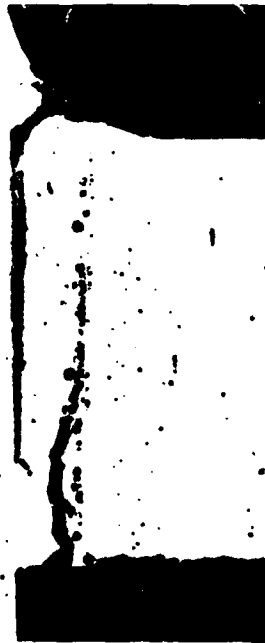




X38 (a) B31367
Fig. 57 Alloy 8E-1 a) before



X38 (b) B31372
b) after etching



X42 B31368
Fig. 58 Alloy 8E-4. Showing
cracking at interface.

Isothermal Exposure of As-Cast Braze Alloys in air



Fig. 59 X200 B31398
Alloy 1A-1 after 1000h/1100°C



Fig. 60 X200 B31399
Alloy 1A-2 after 1000h/1100°C



Fig. 61 X200 B31400
Alloy 1A-3 after 1000h/1100°C

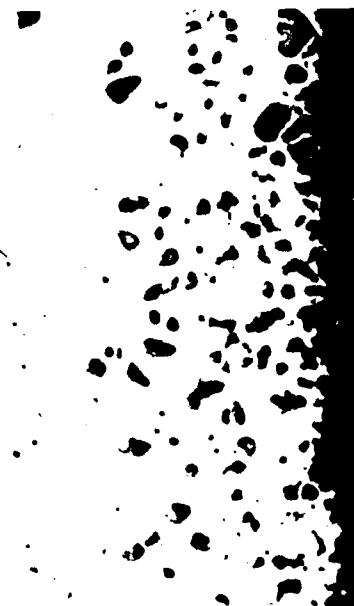


Fig. 62 X200 B31401
Alloy 1A-4 after 1000h/1100°C

Isothermal Exposure of As-Cast Braze Alloys in air



Fig. 63 B31406
Alloy 1A-9 after 1000h/1100°C



Fig. 64 X200 B31391
Alloy 8E-1 after 1000h/1100°C



Fig. 65 X200 B31397
Alloy 8E-2 after 1000h/1100°C

Isothermal Exposure of As-Cast Braze Alloys in air



Fig. 66 X100 B31396
Alloy 8E-3 unexposed



Fig. 67 X100 B31395
Alloy 8E-3 after 1000h/1100°C



Fig. 68 X200 B31393
Alloy 8E-3 after 1000h/1100°C



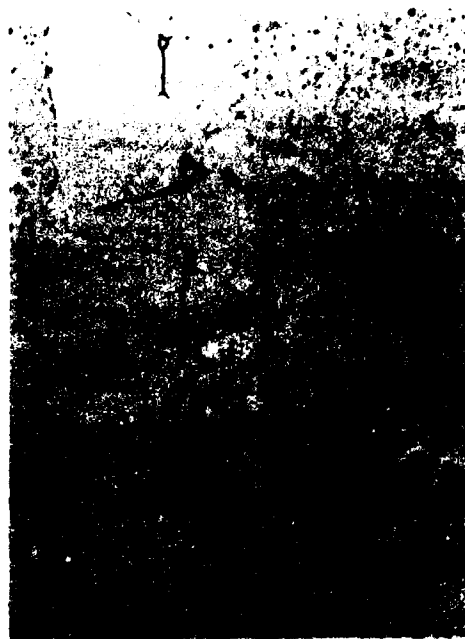
Fig. 69 X200 B31394
Alloy 8E-5 after 1000h/1100°C



Fig. 70
Radiographs of double-lap specimens with alloy 1A at top and
commercial B Ni-1A ductile foil below.



X1000 B31382
Fig. 71 Interface between MA956 (left)
and alloy 1A in brazed joint.



500X B31383
Fig. 72 As Fig. 71 after 1000h/1100°C
exposure.



X500 B31384
Fig. 73 Interface between MA956 (left)
and alloy 4E in brazed joint.



X500 B31385
Fig. 74 As Fig. 73 after 1000 hr/1100°C
exposure.

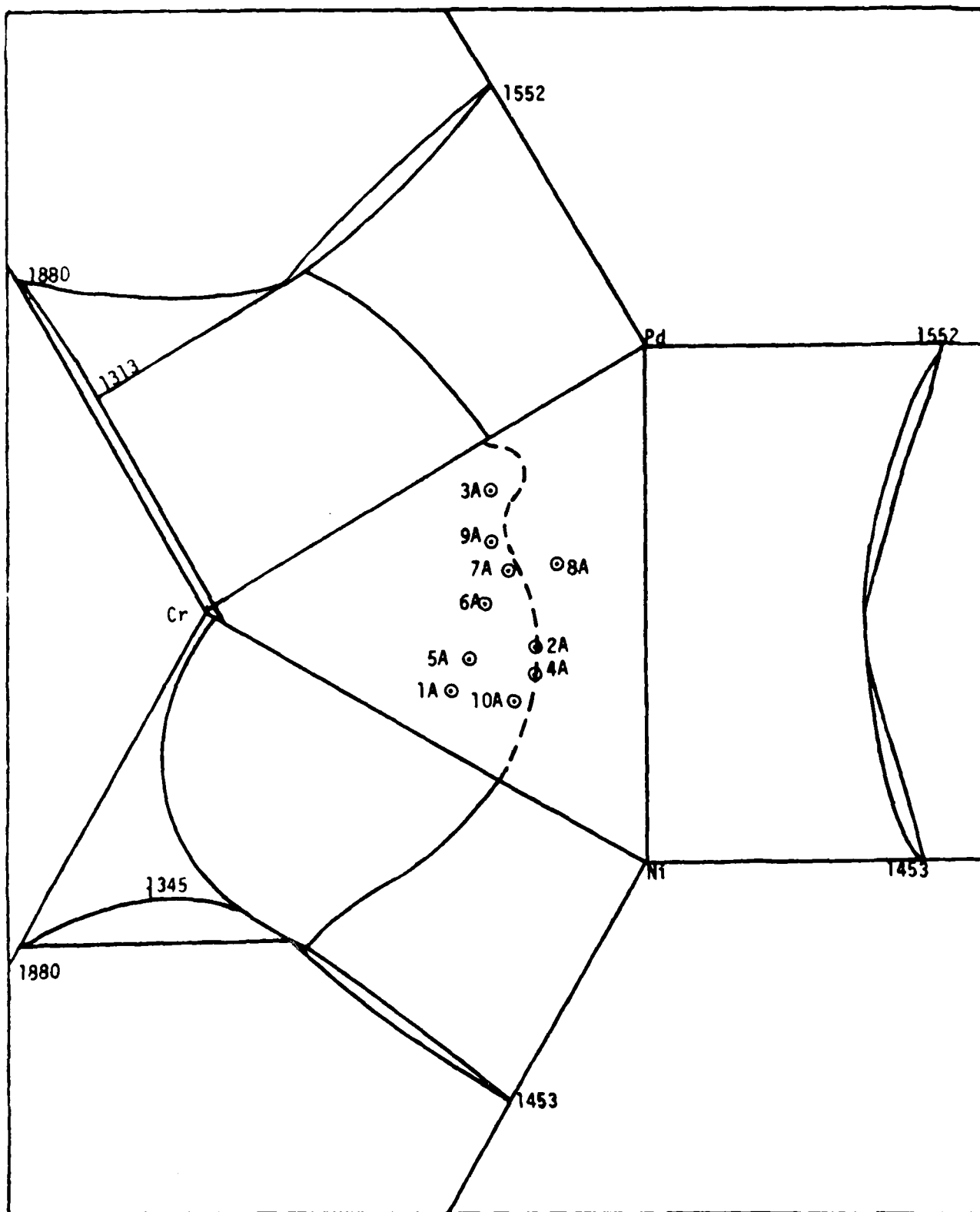


FIG. 75 Ni-Cr-Pd Ternary diagram showing limit of 2-phase field and corresponding position of alloys studied.

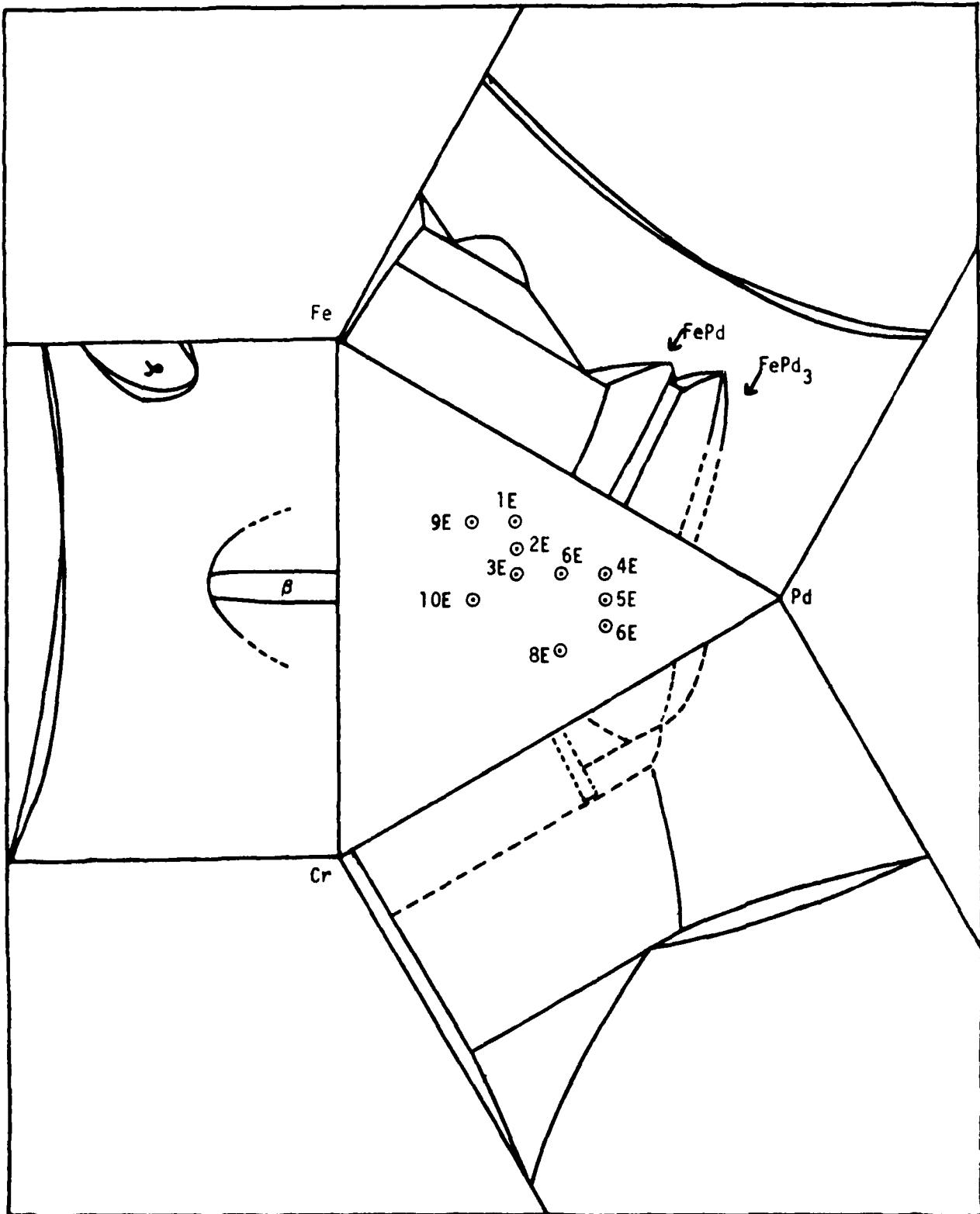
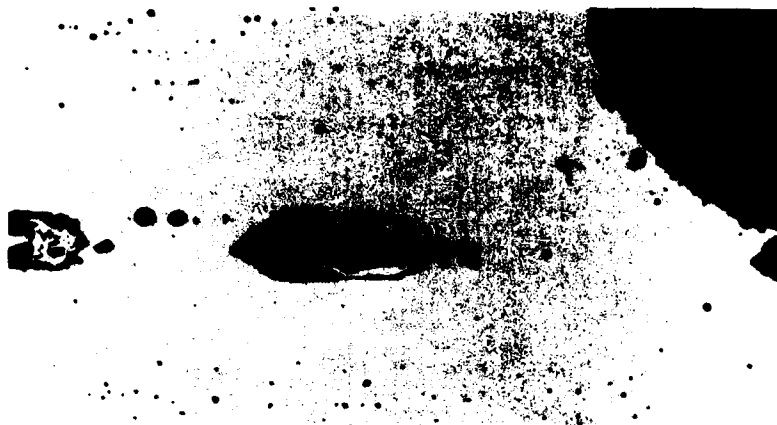


FIG. 76 Fe-Cr-Pd Diagram showing binaries and position of alloys studied.



B.32333 X50
 Fig. 77 Section through braze 1 A-9 after 1000hr/1100°C/
 air exposure. The braze fillet is on the right
 and extensive porosity is present in the braze.
 This porosity was present before exposure.



B.32335 X50
 Fig. 78 Section through braze 1 A-5 after 1000hr/1100°C/
 air exposure. There is very little oxidation
 at surface of fillet (on right) but pre-existing
 porosity in the braze detracts from its quality.



B.32336

X50

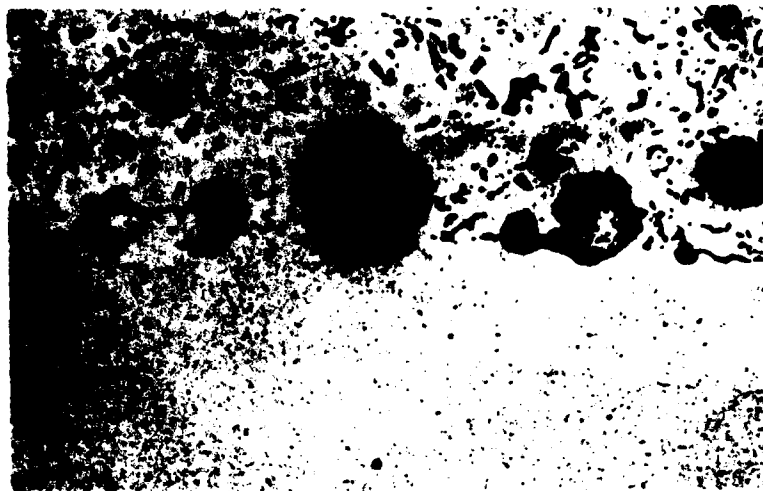
Fig. 79 Section of braze 1 A-3 after 1000hr/1100°C/air exposure showing extensive oxidation associated with pre-existing porosity.



B.32323

X50

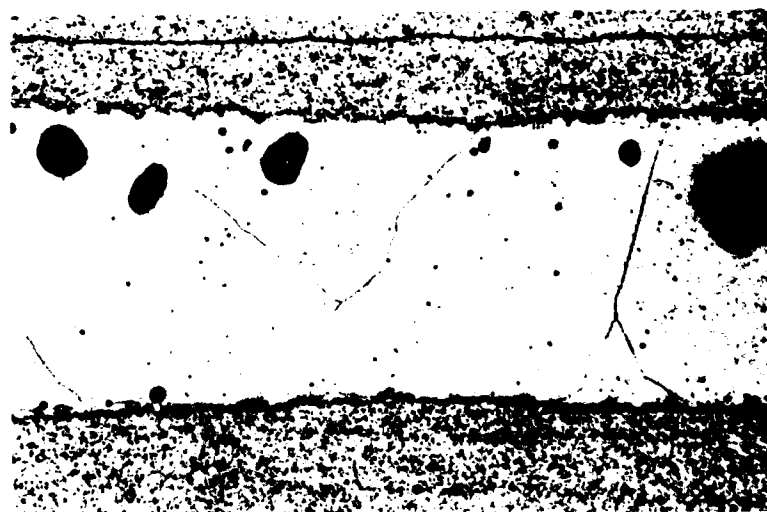
Fig. 80 Section of braze TD-6 after 1000hr/1100°C/air exposure showing very large pre-existing pores but little oxidation at surface of fillet.



B.32396

X200

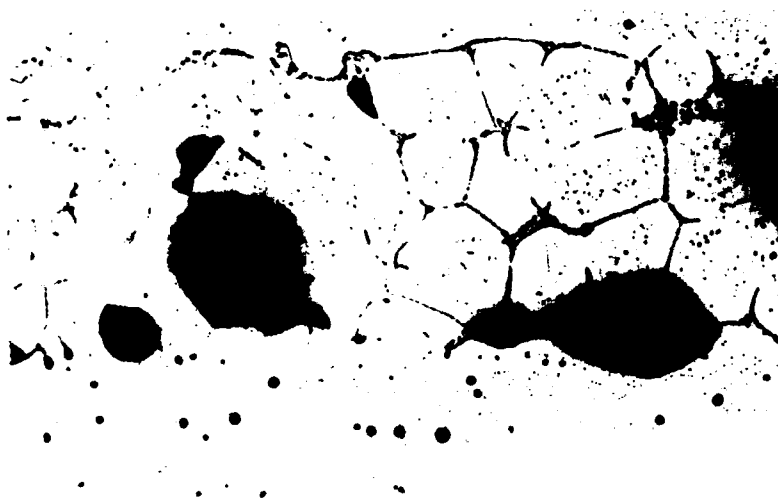
Fig. 81 Braze 1 A-5 after 1000hr/1100°C/air exposure showing sound braze/IN-956 interface except for pre-existing porosity. The braze metal has developed into a coarse 2-phase structure.



B.32400

X200

Fig. 82 Braze TD-6 after 1000hr/1100°C/air exposure showing sound interface with parent metal.



B.32378

X200

Fig. 83 Braze 1 A-3 before exposure.



B.32381

X200

Fig. 84 Braze 1 A-3 after exposure (1000h/1100°C)
showing coarsening of 2-phase structure.



B.32377

X200

Fig. 85 Braze 1 A-9 before exposure.



B.32376

X200

Fig. 86 Braze 1 A-9 after exposure 1000h/1100°C.

CYCLIC OXIDATION - 1000h/1100°C

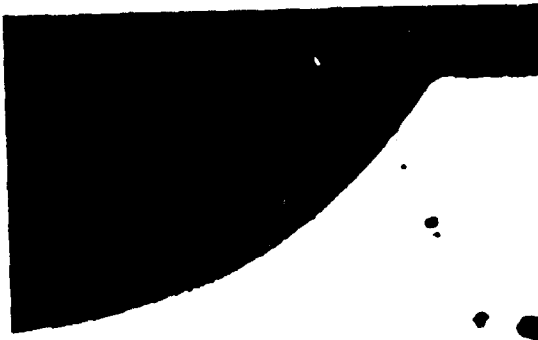


Fig. 87 X25 VC3089
1A1 As-Brazed

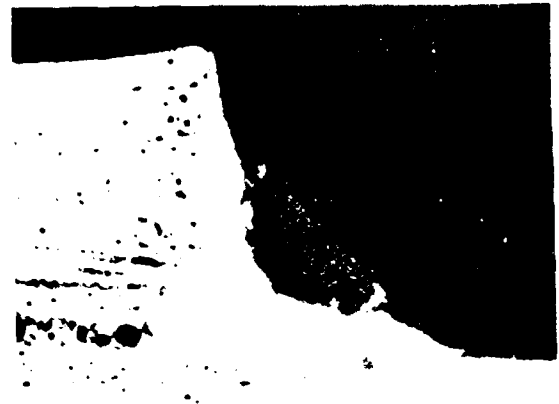


Fig. 88 X25 VC3090
1A1 After Cyclic Test



Fig. 89 X25 VC3091
1A2 As-Brazed



Fig. 90 X25 VC3092
1A2 After Cyclic Test



Fig. 91 X25 VC3093
1A2 As-Brazed



AD-A118 252

WIGGIN ALLOYS LTD HEREFORD (ENGLAND)

F/G 11/6

DEVELOPMENT OF A BRAZING ALLOY FOR THE MECHANICALLY ALLOYED HIG--ETC(U)

SEP 81 W E MORGAN, P J BRIDGES

F49620-79-C-0008

UNCLASSIFIED

TR-3381

AFWAL-TR-81-4093

NL

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4
SYNCHROZ



END

DATE

FILED

9 82

DTIC

CYCLIC OXIDATION - 1000h/1100°C



Fig. 93
LA5 As-Brazed

X25

VC3095

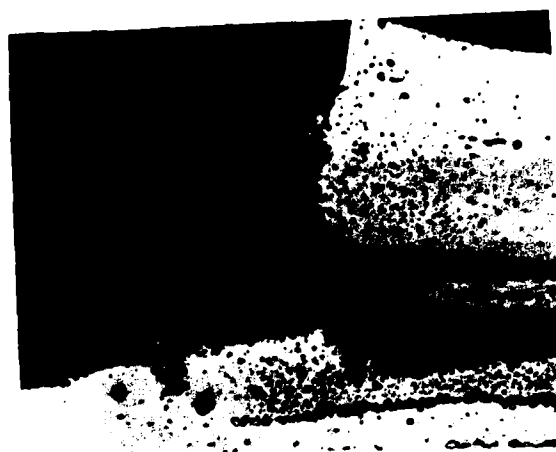


Fig. 94
LA5 After Cyclic Test

X25

VC3096



Fig. 95
LA9 As-Brazed

X25

VC3097



Fig. 96
LA9 After Cyclic Test

X25

VC3098

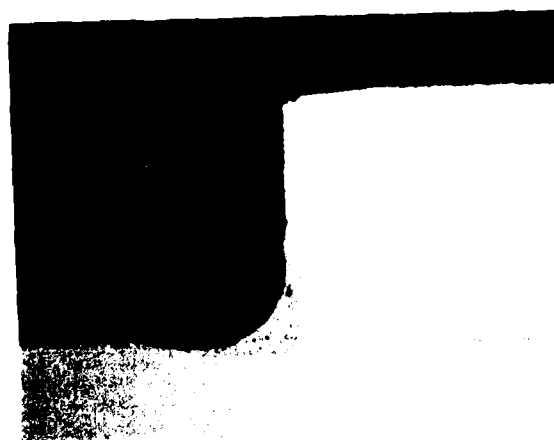


Fig. 97
BNi-LA As-Brazed

X25

VC3087

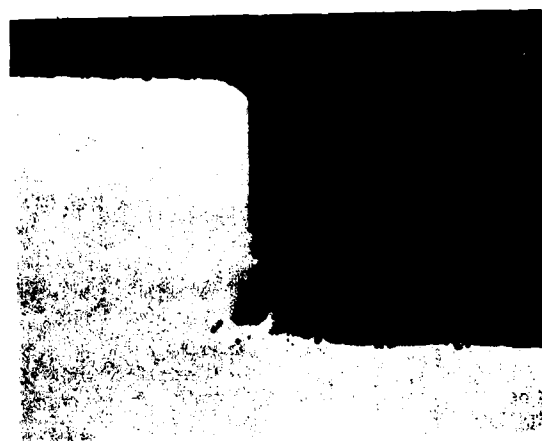


Fig. 98
BNi-LA After Cyclic Test

X25

VC3088

CYCLIC OXIDATION - 1000h/1100°C

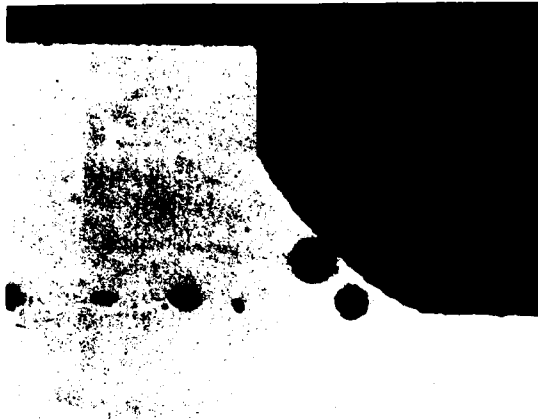


Fig. 99
TD6 As-Brazed

X25

VC3083

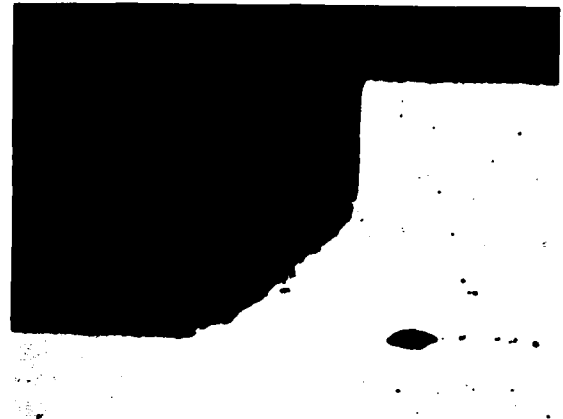


Fig. 100
TD6 After Cyclic Test

X25

VC3084

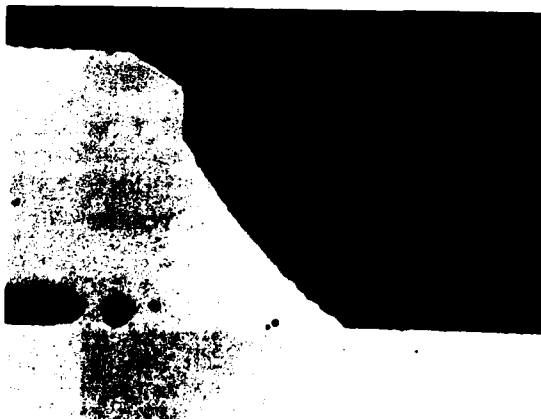


Fig. 101
TD20 As-Brazed

X25

VC3085



Fig. 102
TD20 After Cyclic Test

X25

VC3086